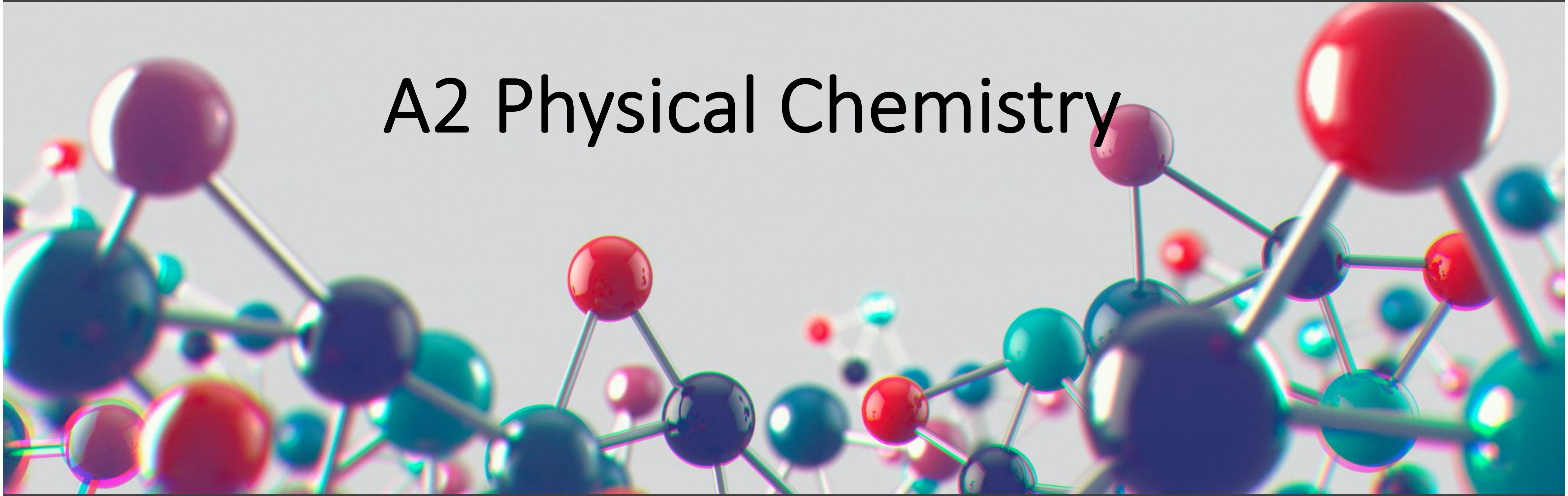
A2 Physical Chemistry



Equilibrium Constant

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Dynamic Equilibrium - Recap

A **reversible process** can move in either direction depending on the conditions.

Most physical processes are easily reversible (e.g. freezing and melting substances.

Many chemical reactions are irreversible under ordinary conditions, but most reactions can be reversed under extreme conditions.

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

A reversible reaction will reach a dynamic equilibrium if sufficient time is allowed for the forward and reverse reactions to reach the same rate

A dynamic equilibrium exists when the forward rate of reaction equals the reverse rate of reaction. It occurs in a closed system and there is no change in overall macroscopic properties (eg temperature, pressure, concentration) .

Reaching Dynamic Equilibrium

Initially, when $H_{2(g)}$ and $N_{2(g)}$ are mixed there is no $NH_{3(g)}$ is present.
Therefore the forward rate of reaction is much faster than the reverse.

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Since rate is proportional to concentration

As the concentration of $NH_{3(g)}$ increases, the backward rate increase.
As the concentrations of $N_{2(g)}$ and $H_{2(g)}$ decrease, the forward rate decreases.

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Equilibrium is reached when
The rate of the forward reaction = The rate of the backward reaction

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

At Dynamic Equilibrium

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

There is no overall change in the concentrations of the reactants and products.

However the reaction has not stopped.

The forward reaction of $3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$

Is happening at the same rate as $2NH_{3(g)} \rightarrow 3H_{2(g)} + N_{2(g)}$

Le Chatelier's Principle

When a system in dynamic equilibrium is subjected to a change in conditions, the equilibrium will shift in the direction that minimises the change.

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

ΔH = Exothermic

Changing concentration

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Le Chatelier's predicts that the equilibrium will shift to reduce the concentration of H_2. Therefore the equilibrium position will shift to the right.

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4 moles

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

4 moles

2 moles

Le Chatelier's predicts that the equilibrium will shift to reduce any changes in pressure.

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$H_2(g)$

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Increase in pressure equilibrium shifts to right hand side

Changing concentration

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Changing Pressure

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4 moles 2 moles

Le Chatelier's predicts that the equilibrium will shift to reduce any changes in pressure.

Decrease in pressure equilibrium shifts to left hand side

Increase in pressure equilibrium shifts to right hand side

Changing Temperature

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

ΔH = Exothermic

Changing Temperature

Exothermic

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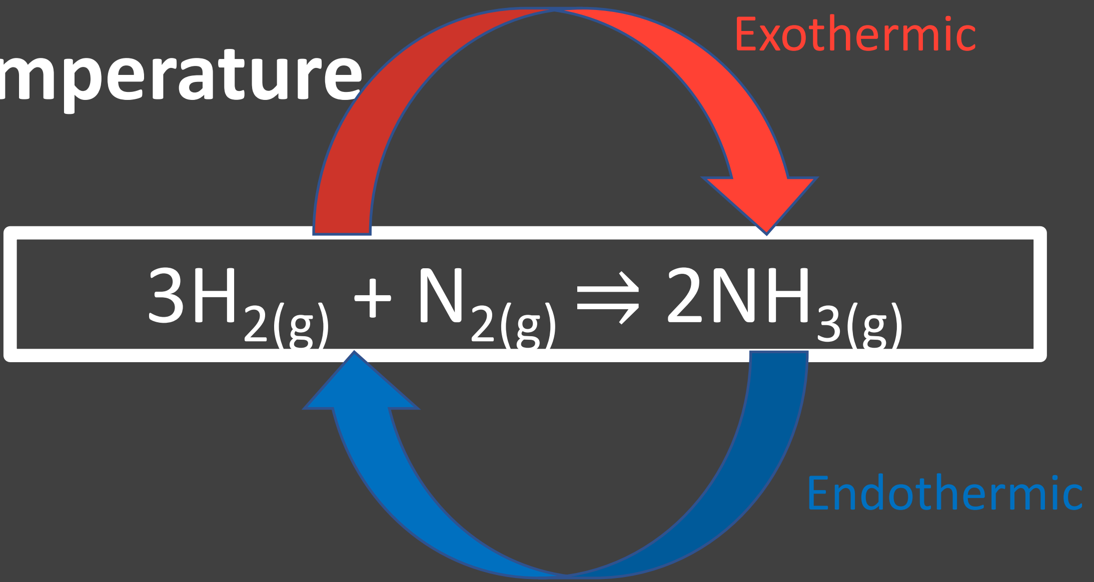
Changing Temperature



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ΔH = Exothermic

Changing Temperature

Exothermic

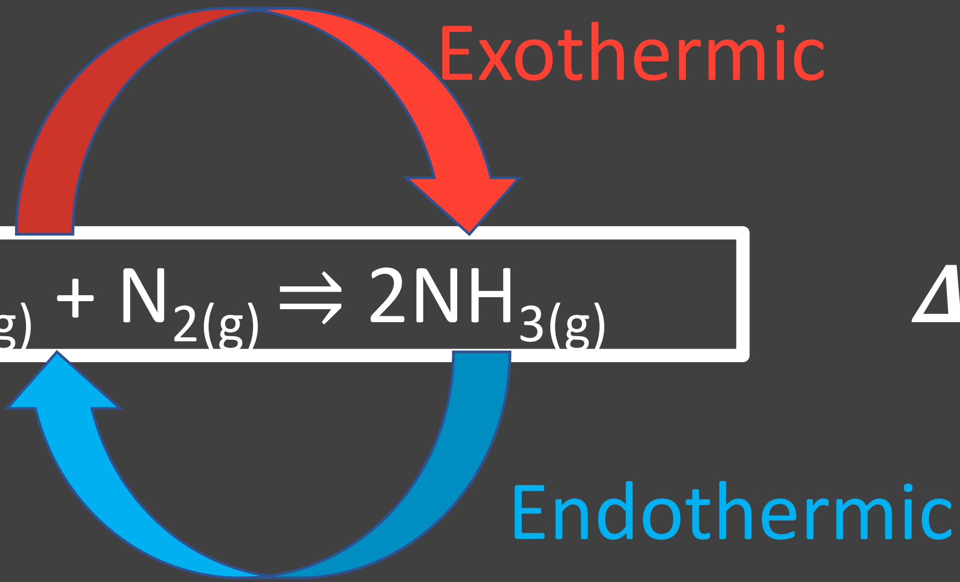
$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Endothermic

ΔH = Exothermic

Le Chatelier's predicts that the equilibrium will shift to reduce any change in temperature.

Changing Temperature



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

ΔH = Exothermic

If the temperature is decreased, the reaction will shift in the exothermic reaction.

If the temperature is increased, the reaction will shift in the endothermic reaction.

The Equilibrium Constant

Le Chatelier's principle is useful in making qualitative predictions.

The Equilibrium Constant, K_c, allows chemists to make quantitative predictions.

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*The **equilibrium constant, Kc**, is the ratio of*

*the **equilibrium** concentrations of products over*
*the **equilibrium** concentrations of reactants*
each raised to the power of their stoichiometric coefficients.

The Equilibrium Constant

K_c in homogeneous equilibria –everything is in the same phase e.g. gaseous phase

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Equilibrium constant → $K_c =$

In terms of concentration

The Equilibrium Constant

K_c in homogeneous equilibria –everything is in the same phase e.g. gaseous phase

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

Equilibrium constant →

$$K_c = \frac{\quad}{\quad}$$

In terms of concentration →

The Equilibrium Constant

K_c in homogeneous equilibria –everything is in the same phase e.g. gaseous phase

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

Equilibrium constant

$$K_c = \frac{[NH_{3(g)}]^2}{[H_{2(g)}]^3[N_{2(g)}]}$$

In terms of concentration

The Equilibrium Constant

K_c in heterogenous equilibria –things are in different phases e.g. gaseous and solid phases.

Kc does not include any term for a solid or liquid in the equilibrium expression.

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{(g)}$$

$$K_c = \frac{[H_{2(g)}][CO_{(g)}]}{[H_2O_{(g)}]}$$

The Equilibrium Constant

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$K_c = [CO_{2(g)}]$$

The Equilibrium Constant

The equilibrium constant always has the same value (provided you don't change the temperature), irrespective of the amounts of reactants and products you started with.

It is also unaffected by a change in pressure or whether or not you are using a catalyst.

The larger the value of K_c, the higher the theoretical yield of products, so an efficient reaction will have a large K_c value.

If the forward reaction is **exothermic** raising the temperature **decreases the value of K.** The equilibrium moves to the left, i.e. in the **endothermic** direction, to lower the temperature, minimising the change.

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