

## Le Chateliers's Principle

states that if an 'instantaneous' change is imposed on an equilibrium, the position of the equilibrium will further change to minimise the 'enforced' change.

### Rule 1 - Temperature and energy changes

1a. Raising the temperature favours the endothermic direction ( $\Delta H +ve$ ). The system absorbs the heat energy from the surroundings to try to minimise the temperature increase.

1b. Decreasing the temperature favours the exothermic direction ( $\Delta H -ve$ ). The system releases heat energy to the surroundings to try to minimise the temperature decrease.

### Rule 2 - Gas pressure changes at constant temperature

2a. Increasing the pressure favours the side of the equilibrium with the least number of gaseous molecules as indicated by the balanced symbol equation. The system attempts to reduce the number of gas molecules present to reduce the pressure increase.

2b. Decreasing the pressure favours the side of the equilibrium with the most number of gaseous molecules as indicated by the balanced symbol equation. The system attempts to increase the number of gas molecules to minimise the pressure decrease.

NOTE:

a) States symbols (g/l/s/aq) are particularly important when considering equilibrium equations, *if no (g) the pressure rule doesn't apply since solids and liquids are virtually incompressible.*

b) *Rule 2 ONLY applies to a reaction with one or more gaseous reactants or products because pressure has no real effect on the 'concentration' on the virtually incompressible liquids or solids.*

c) *If there is NO net change in the number of gas molecules, gas pressure has NO effect on the position of the equilibrium, though pressure increase effectively increases gas concentration so both the forward and backward reactions will be speeded up.*

### Rule 3 - Concentration changes at constant temperature

3a. If the concentration of a reactant (on the left) is increased, then some of it must change to the products (on the right) to maintain a balanced equilibrium position.

3b. If the concentration of a reactant (on the left) is decreased, then some of the products (on the right) must change back to reactants to maintain a balanced equilibrium position.

This means if you change ANY concentration, all the other concentrations must change too. Also, any net concentration changes must comply with the  $K_c$  equilibrium expression.

### Rule 4 - Using a catalyst

A catalyst does NOT affect the position of an equilibrium.

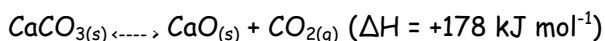
BUT it does enable you get to the point of equilibrium faster!

A catalyst speeds up both the forward and reverse reactions by providing a mechanistic pathway with a lower activation energy, but there is no way it can influence the final 'balanced' concentration ratios.

The importance of a catalyst lies with economics of chemical production e.g. bringing about reactions with high activation energies at lower temperatures and so reducing energy requirements and time, and both reductions save money!

### **Example 1**

The thermal decomposition of calcium carbonate (limestone) to make calcium oxide (quicklime):



**Rule 1** - temperature and energy change

Increasing temperature favours the .....thermic direction (to the ..... ) so more quicklime is formed.

**Rule 2** - gas pressure

Decreasing the pressure of carbon dioxide ....creases the yield of quicklime.

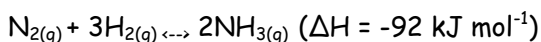
**Rule 3** - concentration

Not applicable to the ..... because you can't decrease or increase the concentration of a solid but you can reduce the concentration of ..... by removing the gases to increase the yield of quicklime.

**Rule 4** - catalyst: Not applicable.

### **Example 2**

The synthesis of ammonia: nitrogen + hydrogen → ammonia (**Haber process**)



**Rule 1** - temperature and energy change

The forward, and desirable reaction, to form ammonia, is ....thermic, so .....creasing the temperature favours its formation.

**Rule 2** - gas pressure

....crease in pressure favours ammonia formation since 4 mol of gaseous reactants ==> 2 mol gaseous products.

**Rule 3** - concentration: In terms of enforced change => system response

Increasing nitrogen ==> ....creases hydrogen and ...creases ammonia.

Increasing hydrogen ==> .....creases nitrogen and ...creases ammonia.

Decreasing ammonia ==> .....creases nitrogen and ....creases hydrogen.

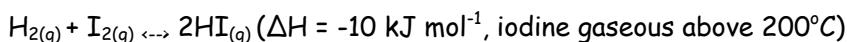
Decreasing nitrogen ==> ....creases hydrogen and ....creases ammonia.

Decreasing hydrogen ==> ....creases nitrogen and ....creases ammonia.

**Rule 4** - catalyst: An **iron oxide** catalyst is used, time = money for industrial chemical production!

### **Example 3**

The formation of hydrogen iodide from hydrogen and iodine:



**Rule 1** - temperature and energy change

Increasing temperature favours the ..... reaction, i.e. ....creases the endothermic decomposition of hydrogen iodide.

**Rule 2** - gas pressure

No effect on position of equilibrium, because.....

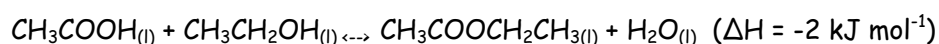
**Rule 3** - concentration

if more iodine was added to a constant volume container, the hydrogen concentration would ....crease as some reacts with added iodine to give more hydrogen iodide as the system tries to minimise the iodine increase.

**Rule 4** - catalyst: Not applicable.

### **Example 4**

Esterification: e.g. ethanoic acid + ethanol → ethyl ethanoate + water



**Rule 1** - temperature and energy change

....crease in temperature favours the ester formation (ethyl ethanoate, forward reaction)

**Rule 2** - gas pressure: (?).....

**Rule 3** - concentration

Sometimes it is desirable to add a large excess of the ..... to ensure most of the acid is converted into ester.

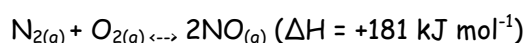
**Rule 4** - catalyst

The forward esterification reaction is catalysed by acids e.g. a few drops of **conc. sulphuric acid**.

The reverse reaction i.e. hydrolysis of the ester back to the acid and alcohol is catalysed by dilute acids.

### **Example 5**

The formation of nitrogen(II) oxide.



**Rule 1** - temperature and energy change

Increase in temperature favours the ..... reaction.

This reaction does not happen at room temperature but is formed at the high temperatures in car engines.

Unfortunately when released through the car exhaust, it cools to normal temperatures when NO irreversibly reacts with oxygen in air to form nitrogen(IV) oxide, NO<sub>2</sub>, which is acidic, a lung irritant and a reactive free radical molecule involved in the chemistry of photochemical smog not good!

**Rule 2** - gas pressure

Pressure does not affect the position of the equilibrium since .....

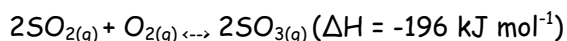
**Rule 3** - concentration

The concentration of nitrogen is high from air, but although the concentration of oxygen is low in the exhaust gases, there is sufficient present in the combustion process to ensure a small % of NO is formed.

**Rule 4** - catalyst: Not applicable.

### **Example 6**

The oxidation of sulphur dioxide to sulphur trioxide  
(e.g. in the **Contact** Process for manufacturing sulphuric acid)



**Rule 1** - temperature and energy change

The exothermic formation of sulphur trioxide is favoured by ..... temperature.

**Rule 2** - gas pressure

..... pressure favours a higher yield of sulphur trioxide as 3 gas moles  $\Rightarrow$  2 gas moles, though 1-2 atm is used in practice because the equilibrium is already so far to the right (about 99%).

**Rule 3** - concentration

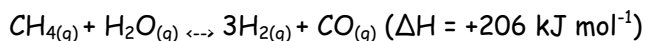
Air is used as the source of oxygen and, despite its dilution with nitrogen, the concentration of oxygen is high enough to move the equilibrium very much to the .....

**Rule 4** - catalyst

A **vanadium(V) oxide**,  $\text{V}_2\text{O}_5$ , catalyst ensures the high yield of 99%  $\text{SO}_3$  is attained fast, but no more!

### **Example 7**

One way to produce hydrogen for the Haber synthesis of ammonia is to react methane gas with steam.



**Rule 1** - temperature and energy change

.....crease in temperature favours the endothermic formation of hydrogen (and carbon monoxide).

**Rule 2** - gas pressure

For the desired forward reaction, 2 mol of reactant gases  $\Rightarrow$  4 mol of product gases, so the increase in product volume is favoured by ..... pressure.

**Rule 3** - concentration

Theoretically increase in methane and steam concentrations will increase the hydrogen concentration, but this essentially means increasing pressure favouring the reverse reaction, so you might not gain as much hydrogen as you like to!

**Rule 4** - catalyst

A **nickel** catalyst is used, but cannot affect the yield.