AS91166
Chemical Equilibrium

Le Chatelier's Principle: **"When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change." Or "any change made to a system in equilibrium results in a shift of the equilibrium in the direction that minimises the change."**

When a chemical equilibrium is established . . .

- the reaction is dynamic - it is moving forwards and backwards
- the rates of forward and backward reactions are equal
- both the reactants and the products are present at all times
- the equilibrium can be approached from either side
- concentrations of reactants and products remain constant

The Equilibrium Law

"If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant"

$$aA + bB \rightleftharpoons cC + dD$$

then

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

Note:
Products on top!
No "+" signs!!

K_c = is known as the equilibrium constant, and [ ] = equilibrium concentration, in mol L^{-1}. K_c is NOT affected by changes in concentration, pressure or addition of a catalyst but K_c is affected by a change in temperature.

The size of K_c

If K_c is very large (greater than 10^3) the concentration of product is high compared to that of reactants (as the product concentration is on top of the ratio). If K_c is very small (less than 10^{-3}) the concentration of reactant is high compared to that of products (as the reactant concentration is on the bottom of the ratio.)

Factors affecting equilibrium position

Concentration. $aA + bB \rightleftharpoons cC + dD$

- increase [A] or [B], equilibrium position moves to the right
- decrease [A] or [B], equilibrium position moves to the left
- increase [C] or [E], equilibrium position moves to the left
- decrease [C] or [D], equilibrium position moves to the right

Pressure

Increase in pressure favours a move to the side with fewer gaseous molecules / moles of gas.
Decrease in pressure favours a move to the side with more gaseous molecules / moles of gas.

Temperature

An increase in temperature favours the endothermic reaction.
A decrease in temperature favours the exothermic reaction.

Reminder: $aA + bB \rightleftharpoons cC + dD$: +ΔH means that the forward reaction is endothermic and the backward reaction is exothermic.

$aA + bB \rightleftharpoons cC + dD$: -ΔH means that the forward reaction is exothermic and so this backward reaction is endothermic.

Catalysts

These do not affect the position of equilibrium but the rate at which equilibrium is reached.

The Haber Process – the production of AMMONIA

The Haber Process combines nitrogen from the air with hydrogen obtained from methane gas into ammonia, NH3. The reaction is reversible and the production of ammonia is exothermic.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 : \Delta H = -92 \text{ kJ mol}^{-1}$$

Unfortunately the equilibrium sits firmly on the side of the reactants and so the position of the equilibrium needs to be shifted as far as possible to the right in order to produce the maximum possible amount (yield) of ammonia in the equilibrium mixture.

Temperature - 400 - 450°C

The forward reaction (production of ammonia) is exothermic. According to Le Chatelier's Principle, this will be favoured by a low temperature. The system would respond by shifting the position of equilibrium to the right to counteract this by producing more heat.

But… the lower the temperature used, the slower the reaction becomes. A manufacturer is trying to produce as much ammonia as possible per day. A compromise temperature of 400 - 450°C is produces ammonia in the equilibrium mixture (even if it is only 15%), in a very short time.

Pressure - 200 atmospheres

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ There are 4 molecules on the left-hand side of the equation, but only 2 on the right. According to Le Chatelier's Principle, an increase in pressure will favour the reaction which produces fewer molecules (and causes pressure to fall).

A pressure of 200 atmospheres is used. This is NOT an amazing high pressure but very high pressures are very expensive. It needs extremely strong pipes and containment vessels to withstand the very high pressure. Additionally high pressures cost a lot to produce and maintain. That means that the capital and running costs of your plant would be very high if higher pressures were used.

Catalyst - iron catalyst

A catalyst has no effect whatsoever on the position of the equilibrium & does not alter the % of ammonia in the equilibrium mixture. Its only function is to speed up the reaction. Without a catalyst the reaction is so slow that virtually no reaction happens in any sensible time. A finely-divided iron catalyst is used.

Removing the ammonia - ammonia liquefied

Ammonia is easily liquefied & piped off. The nitrogen and hydrogen remain as gases & can be recycled. Removal of the ammonia shifts the position of equilibrium to the right, producing a higher percentage of ammonia.

ADDITIONAL NOTES

Equilibrium Constant, *K*

Constants will be dimensionless, i.e. have no units, in keeping with current IUPAC conventions. They include:

K_c - General equilibrium constant in which the equilibrium composition is expressed in terms of concentration of species

K_w - Dissociation constant of water

Equations for Chemical Reactions

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ fwd reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ equilibrium

Calculations involving K_c

At a particular temperature, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.

For this eqm. (at this temp.) the value of K_c is 280. If the following three gases are mixed in a 1L container, $[SO_2]$ = 0.500 mol, $[O_2]$ = 0.100 mol, $[SO_3]$ = 0.700 mol, we can justify whether the reaction would proceed in the fwd OR rev. direction when the gases are mixed.

$[SO_3]^2 / [SO_2]^2 . [O_2] = (0.7)^2 / (0.5)^2 . (0.1) = 19.6$

This is less than K_c at equilibrium (280) so reactants > products at this stage. The equilibrium will move in the forward direction to produce more product, SO_3, and hence allow the mixture to reach equilibrium, the value approaching K_c for this reaction.