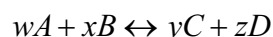


Equations:

Given the equation at equilibrium :



The following is true :

$$\text{Rate}(f) = k_f [A]^w [B]^x$$

$$\text{Rate}(r) = k_r [C]^y [D]^z$$

$$\therefore \text{Rate}(f) = \text{Rate}(r) \text{ and } k_c = \frac{k_f}{k_r}$$

$$\therefore k_c = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

$$\text{Multiply eq}^n \text{ by } n : k_{\text{new}} = (k_{\text{old}})^n$$

$$\text{Divide eq}^n \text{ by } n : k_{\text{new}} = \frac{1}{\sqrt[n]{k_{\text{old}}}}$$

$$\text{Adding eq}^n : k_{\text{new}} = k_1 \times k_2 \times k_3 \dots k_n$$

$$\text{Subtracting eq}^n : k_{\text{new}} = \frac{k_1}{k_2}$$

$$\text{For gases : } k_p = k_c (RT)^{\Delta n_{(\text{gas})}}$$

Definitions:**1- Equilibrium**

A state in which all change has ceased (static) or all change appears to have ceased (dynamic).

2- Dynamic Equilibrium

Forward and reverse rates of reaction are equal. Also, macroscopic properties do not change (e.g. pressure, temperature).

3- Saturated Solution

No more solvent can be dissolved in the solute.

Key Concepts:**Characteristics of a System at Equilibrium (P. 3)**

- 1- Closed system (no adding or removing)
- 2- Constant pressure
- 3- Constant temperature
- 4- Constant Colour
- 5- Can be approached from either direction
- 6- Constant concentration (though not necessarily 50/50)
- 7- Microscopic properties are *continuous*

Heat Content

Assume $x > 0$

If $\Delta H^\circ_{\text{rxn}} = +x$, then endothermic reaction.

If $\Delta H^\circ_{\text{rxn}} = -x$, then exothermic reaction

Factors that Affect Equilibrium (P. 3-5)

Factor	Effect on Temperature	Rate of Reaction	Effect on Equilibrium
Concentration +++ Reactant +++ Product --- Reactant --- Product	None None None None	Faster Faster Faster Faster	Right Left Left Right
Temperature +++ ---	++ --	Faster Slower	Favour endo. Favour exo.
Pressure¹ +++ ---	None None	Faster Slower	--- mol. favoured +++ mol. favoured
Catalyst	None	Faster	None
Volume +++ --- +++ Noble Gas	None None None	Faster Faster None	+++ mol. favoured --- mol. favoured None

Le Chaterliers Prcinciple (P. 6-7)

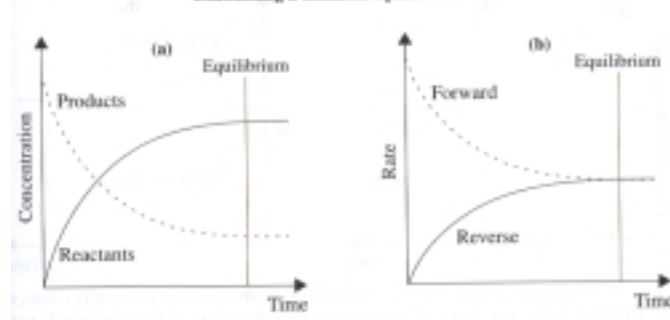
“If an equilibrium is subjected to a change, processes occur that tend to counteract partially the imposed change.”

The Equilibrium Constant (K_c)

- 1- Varies depending on temperature.
- 2- Units vary depending on equation.
- 3- Large value \rightarrow predominantly forward reaction
- 4- Small value \rightarrow predominantly reverse reaction
- 5- Only gases and aqueous solutions are taken into account
Why? Solids do not vary in concentration.
- 6- Does not vary with concentration or changes in pressure.

Be able to interpret equilibrium graphs:

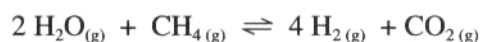
Figure 8.1 – The change of concentration (a) and rate of reaction (b) with time in establishing a chemical equilibrium



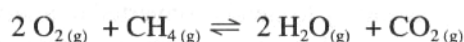
¹ Note, no change if same number of molecules on both sides of equation.

THE HABER PROCESS

The Haber process involves the direct combination of nitrogen and hydrogen to produce ammonia. Firstly it is important to obtain the reactants in an economically viable manner. Hydrogen can, for example be produced by the electrolysis of water and nitrogen by the fractional distillation of liquid air, but both of these would be prohibitively expensive. Instead steam is reacted with excess methane, from natural gas, in a number of stages over various heated catalysts to finally produce a mixture of hydrogen, carbon dioxide and some excess methane.



Air is then added with this and the oxygen reacts with the hydrogen to produce more steam, which then reacts (as above) with the excess methane to form more hydrogen and carbon dioxide. The nitrogen, being inert under these conditions, remains unchanged.



The final result is a mixture of nitrogen, hydrogen and carbon dioxide. The carbon dioxide is then removed by scrubbing with saturated, aqueous potassium carbonate.



This reaction can be reversed by heating the aqueous potassium hydrogencarbonate, so regenerating the carbonate. The result of all of these reactions is to provide a mixture of nitrogen and hydrogen in a 1:3 ratio. This is compressed and passed over a heated iron catalyst where the following equilibrium is established.



The choice of conditions for this equilibrium is critical. It can be seen that the reaction goes from 4 moles of gas to 2 moles of gas, hence a high pressure will favour the formation of the product, as Figure 8.5 confirms. The provision of a high pressure is however expensive, both in terms of the capital cost of providing a plant that will resist high pressures and in terms of the operating costs of compressing gases to high pressures. The final choice will therefore be a compromise pressure that takes into account these factors.

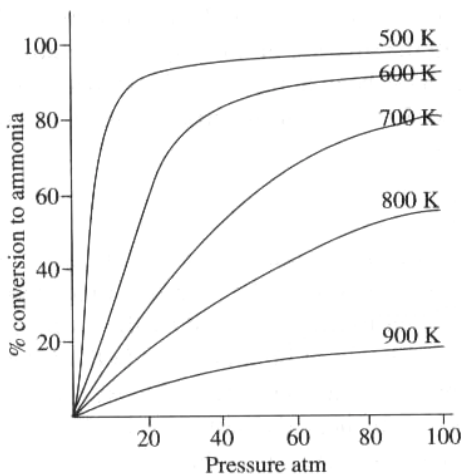
It can be seen from the equation above that the forward reaction is exothermic (ΔH negative), hence a low temperature would favour the products, as can be seen from Figure 8.5. Unfortunately low temperatures result in low rates of reaction so that even though there may be a high proportion of ammonia in the product it may take a long time for the conversion to occur. Again a compromise temperature is chosen so as to produce

Equilibrium

the maximum mass of ammonia per hour. The use of a finely divided catalyst containing iron also increases the reaction rate.

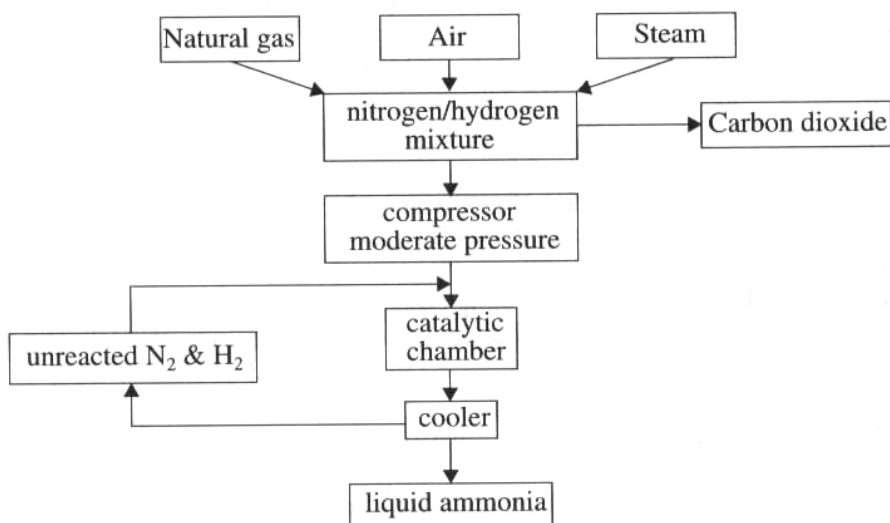
CORE

Figure 8.5 – The effect of conditions on the proportion of ammonia at equilibrium



Typical conditions chosen for the Haber process are pressures in the range 200 – 1000 atm (20 – 100 MPa) and temperatures $\sim 700\text{K}$. The reaction is however not left for sufficient time for equilibrium to be established (remember the reaction rate will decrease as equilibrium is approached – see Figure 8.1) and typically in the converter only about 20% of the nitrogen and hydrogen is converted to ammonia. It would be very uneconomical to waste the unchanged reactants, so the mixture of gases is cooled causing the ammonia to condense (it can hydrogen bond, unlike the reactants) so that it can be separated and the nitrogen and hydrogen recycled. This is shown schematically in Figure 8.6 below:

Figure 8.6 – Schematic diagram for the commercial production of ammonia



Nitrogen is an element vital for plant growth, so the major use of ammonia is the manufacture of fertilizers, such as ammonium salts and urea. It is also used in the manufacture of nitrogen containing polymers such as nylon. Ammonia can also be oxidised to produce nitric acid (see the equations below), which is used in the production of explosives such as TNT, dynamite etc. and in the dye industry.

