HABER PROCESS AND PH SCALE

The Haber Process for Ammonia

This is a good example of the application of chemical principles to an industrial process.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

Catalyst

In the absence of a catalyst the nitrogen and hydrogen hardly combine. Anyway, the high temperature needed to make the nitrogen and hydrogen combine would force the equilibrium to the left so little ammonia would be formed. An iron catalyst is used in the Haber process; this allows a fast reaction rate at lower temperature and gives a reasonable yield of ammonia.

Pressure

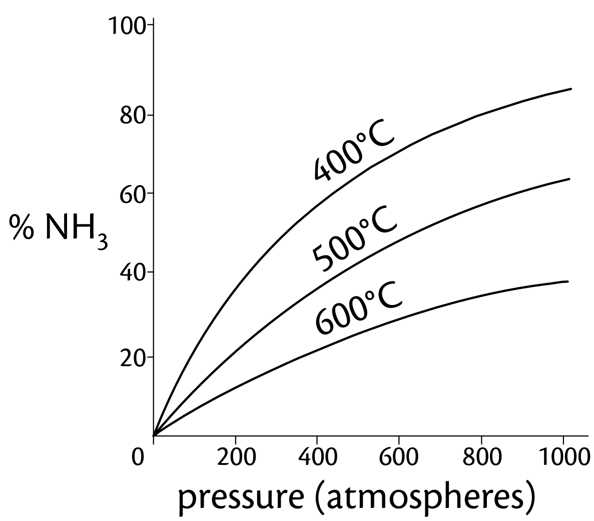
The formation of ammonia gives a decrease in the number of molecules of gas, so a high pressure favours ammonia production. However, plants that operate at high pressure are costly to build and require expensive compressors.

Temperature

A low temperature would give a high equilibrium yield of ammonia. However a low temperature means a slow rate and a long time to come to equilibrium. A higher temperature increases the rate but gives a reduced yield of ammonia. Clearly compromises must be reached between the competing factors which are summarised below.

Condition	Pro (Advantages)	Con (Disadvantages)
high pressure	good equilibrium yield of NH_3	costly to build and operate
low temperature	good equilibrium yield of NH_3 and easy on catalyst	reaction slow to reach equilibrium

The percentage yield of ammonia at various temperatures and pressures is shown on the graph below.



A modern ammonia plant operates at about 80 atmospheres and a temperature of 500K. From the graph we would expect a yield of about 25% ammonia. However, the yield obtained in practice is only about 14%. This is because the time the gases spend in the catalytic converter is too short for equilibrium to be established. It is more economical to remove the ammonia that has formed by cooling it to liquid ammonia and recycling the unreacted nitrogen and hydrogen. Repeated recycling gives a conversion rate of about 98%.

Raw Materials for the Haber Process

The nitrogen comes from the air. The hydrogen comes from syngas manufactured from natural gas and steam.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

An industrial process is obviously more economic if the raw materials are readily available.

Marketability of Ammonia

This is clearly important for any industrial product. There is a large market for ammonia because it is further converted into fertilisers, nitric acid and nylon.

Equilibrium in aqueous solutions

We learned in fourth year that pure water conducts electricity to a slight extent. This is due to the slight dissociation of water molecules as shown by the equilibrium.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium lies very much to the left; only 1 in every 555 million water molecules dissociates.

The pH scale

Dilution of 1 mol l^{-1} HCl

With a pH meter we found that 1 mol l^{-1} HCl had a pH of 0. We took 10 ml of this acid solution and made the volume up to 100ml with distilled water – this is a ten fold dilution and gave us 0.1 mol l^{-1} HCl which had a pH of 1. This dilution was repeated several times.

It is worth remembering that for dilutions such as this, $C_1V_1 = C_2V_2$ where C is the concentration and V is the volume.

Before we look at the full results, note that square brackets are used in chemistry to denote concentration. So $[H^+]$ means "the concentration of H^+ ions" usually measured in mol l^{-1}.

For 0.1 mol l^{-1} HCl $[H^+] = 10^{-1}$ mol l^{-1}

and for 0.01 mol l^{-1} HCl $[H^+] = 10^{-2}$ mol l^{-1} and so on

Results

HCl concentration (mol l^{-1})	$[H^+]$ (mol l^{-1})	pH
1.0	10^{0}	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
0.00001	10^{-5}	5
0.000001	10^{-6}	6
0.0000001	10^{-7}	7

Dilution of 1 mol l^{-1} NaOH

This similar experiment gave these results:

NaOH concentration (mol l^{-1})	$[OH^-]$ (mol l^{-1})	pH
1.0	10^0	14
0.1	10^{-1}	13
0.01	10^{-2}	12
0.001	10^{-3}	11
0.0001	10^{-4}	10
0.00001	10^{-5}	9
0.000001	10^{-6}	8
0.0000001	10^{-7}	7

Ionic Product for Water

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

When pure water dissociates one H^+ ion is produced for every OH^- ion, so

$$[H^+] = [OH^-]$$

From the two previous tables above we can see that at pH 7

$$[H^+] = [OH^-] = 10^{-7} \text{ mol } l^{-1}$$

The ionic product of water, $K_W = [H^+][OH^-] = 10^{-7} \times 10^{-7} \text{ mol}^2 \, l^{-2}$

$= 10^{-14} \text{ mol}^2 \, l^{-2}$

This is a very important relationship. Although we have worked it out for water at pH7, it is true at all pH values.

The crucial fact to remember is that the relationship

$$[H^+][OH^-] = 10^{-14} \text{ mol}^2 \, l^{-2}$$

must be true at all times in aqueous solutions.

The table below (which incorporates the two previous tables) shows the relationship between $[H^+]$, $[OH^-]$ and pH.

Concentration of $H^+_{(aq)}$ (mol l^{-1})	$[H^+]$	pH	$[OH^-]$	Concentration of $OH^-_{(aq)}$ (mol l^{-1})
10	1×10^1	−1	1×10^{-15}	
1	1×10^0	0	1×10^{-14}	
0.1	1×10^{-1}	1	1×10^{-13}	
0.01	1×10^{-2}	2	1×10^{-12}	
0.001	1×10^{-3}	3	1×10^{-11}	
0.000 1	1×10^{-4}	4	1×10^{-10}	
0.000 01	1×10^{-5}	5	1×10^{-9}	
0.000 001	1×10^{-6}	6	1×10^{-8}	
0.000 000 1	$\mathbf{1 \times 10^{-7}}$	**7**	$\mathbf{1 \times 10^{-7}}$	**0.000 000 1**
	1×10^{-8}	8	1×10^{-6}	0.000 001
	1×10^{-9}	9	1×10^{-5}	0.000 01
	1×10^{-10}	10	1×10^{-4}	0.000 1
	1×10^{-11}	11	1×10^{-3}	0.001
	1×10^{-12}	12	1×10^{-2}	0.01
	1×10^{-13}	13	1×10^{-1}	0.1
	1×10^{-14}	14	1×10^0	1
	1×10^{-15}	15	1×10^1	10

Calculating the pH of Solutions

Example 1

What is the pH of a 0.01 mol l^{-1} solution of hydrochloric acid?

$$HCl_{(g)} \longrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

1 mole → 1 mole

$[H^{+}] = 0.01 \text{ mol } l^{-1}$

$= 10^{-2} \text{ mol } l^{-1}$

So the pH = 2

Example 2

What is the pH of a 0.001 mol l^{-1} solution of sodium hydroxide?

$$NaOH \longrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

1 mole → 1 mole

$[OH^{-}] = 0.001 \text{ mol } l^{-1}$

$= 10^{-3} \text{ mol } l^{-1}$

In any aqueous solution:

$[H^{+}][OH^{-}] = 10^{-14} \text{ mol}^{2} \text{ } l^{-2}$

So $[H^{+}] = \dfrac{10^{-14}}{[OH^{-}]}$

$= \dfrac{10^{-14}}{10^{-3}}$

$= 10^{-11} \text{ mol } l^{-1}$

So the pH = 11

Both the examples we have done have shown integral pH values.

In fact the pH scale is continuous running from less than 0 to more than 14, and pH values can be non integral (although you will not do calculations with such values).

Source : http://ciseche10.files.wordpress.com/2013/12/4-chemical-equilibria.pdf