Grade 12 Chemistry

Chemical Systems & Equilibrium

Class 11

Overall Expectations

- Analyze chemical equilibrium processes, and assess their impact on biological, biochemical, and technological systems
- Investigate the qualitative and quantitative nature of chemical systems at equilibrium, and solve related problems
- Demonstrate an understanding of the concept of dynamic equilibrium and the variables that cause shifts in the equilibrium of chemical systems

Chemical Equilibrium

"To what extent does the reaction happen?"

- **Chemical Equilibrium** = the state reached when the rates of the forward and reverse reactions are equal and the concentrations of reactants and products remain constant over time

$$N_2O_4(g) \leftrightarrows 2NO_2(g)$$

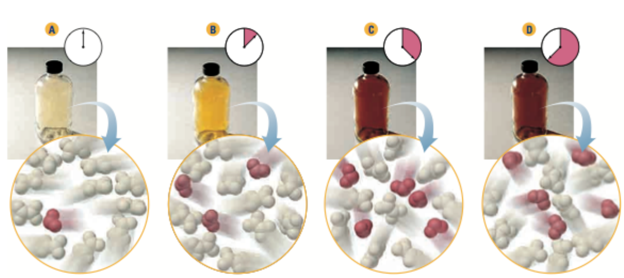
Rate of Forward = Rate of Reverse

Law of Chemical Equilibrium

- At equilibrium, there is a constant ratio between the concentrations of the products and reactants in any change

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

colourless **brown**



- The reaction of dinitrogen tetroxide involves both forward and reverse reactions which are elementary steps

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

colourless **brown**

Forward reaction: $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$ Reverse reaction: $2NO_{2(g)} \rightarrow N_2O_{4(g)}$

Forward rate: $k_f[N_2O_4]$ Reverse rate: $k_f[NO_2]^2$

At equilibrium,

$$\text{Foward rate} = \text{Reverse rate}$$

$$k_f[N_2O_4] = k_r[NO_2]^2$$

$$\frac{k_f}{k_r} = K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant K_{eq}

$$aA + bB \Leftrightarrow cC + dD$$

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

Concentration of products

Concentration of reactants

- Solids and liquids are not included because their concentrations do not change; only include concentrations of gases and aqueous solutions
- Also expressed as K_c for molar concentrations

Checkpoint

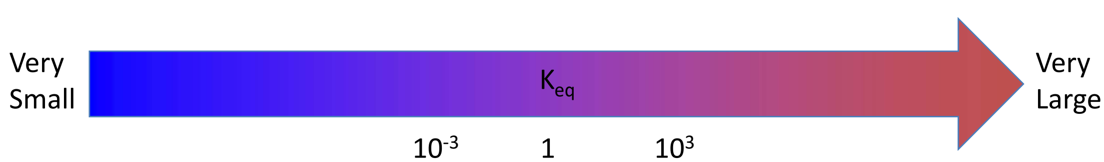
Write the equilibrium equation for the following reactions:

a) $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$

b) $CO_2(g) + C(s) \leftrightarrows 2CO(g)$

c) $4Fe(s) + 3O_2(g) \leftrightarrows 2Fe_2O_3(s)$

- The value of K_{eq} tells you the direction the reaction favours:
  - **K_{eq} < 10^{-3}**, reactants predominate and reaction proceeds hardly at all
  - **K_{eq} from 10^{-3} to 10^{3}**, both reactants and products are present and reaction proceeds
  - **K_{eq} > 10^{3}**, products predominate and reaction proceeds to nearly completion



Checkpoint

$N_2(g) + 3Cl_2(g) \leftrightarrows 2NCl_3(g)$

When the 5.0L equilibrium mixture was analyzed, it was found to contain 0.0070mol of $N_2(g)$, 0.0022mol of $Cl_2(g)$ and 0.95mol of $NCl_3(g)$. Calculate the K_{eq} for this reaction.

Calculating Equilibrium Concentrations

1. Write the balanced equation for the reaction.
2. Under the balanced equation, write the:
   - **I** - Initial concentration
   - **C** - The change in concentration
   - **E** - Equilibrium concentration
3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x

Checkpoint

$H_2(g) + I_2(g) \leftrightarrows 2HI(g)$

At 700K, the K_{eq} = 57.0. If 1.00mol of $H_2(g)$ is allowed to react with 1.00mol of $I_2(g)$ in a 10.0L reaction vessel at 700K, what are the concentrations of $H_2(g)$, $I_2(g)$, HI(g) at equilibrium?

Step 1: $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$

Step 2:

	$H_2(g)$	$I_2(g)$	2HI(g)
Moles (mol)	1.00	1.00	0.00
Volume (L)	10.0	10.0	10.0
Concentration (M)	0.100	0.100	0.00

	$H_2(g)$	$I_2(g)$	2HI(g)
Initial (M)	0.100	0.100	0.00
Change (M)	-x	-x	+2x
Equilibrium (M)	0.100-x	0.100-x	2x

Step 3: Substitute the concentrations into the equation.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(0.100 - x)(0.100 - x)}$$

$$57.0 = \left(\frac{2x}{0.100 - x}\right)^2$$

$$\sqrt{57.0} = \frac{2x}{0.100 - x}$$

$$\pm 7.55 = \frac{2x}{0.100 - x}$$

$$-7.55(0.100 - x) = 2x$$

$$-0.755 = 2x - 7.55x$$

$$x = \frac{-0.755}{-5.55} = 0.136\text{M}$$

$$7.55(0.100 - x) = 2x$$

$$0.755 = 2x + 7.55x$$

$$x = \frac{0.755}{9.55} = 0.079\text{M}$$

The value of *x* cannot exceed 0.10M therefore we can discard *x* = 0.136 M

Equilibrium Concentrations:

$[H_2]$ = 0.100 – *x* = 0.100 – 0.079 = 0.021M

$[I_2]$ = 0.10 – *x* = 0.100 – 0.079 = 0.021M

[HI] = 2*x* = 2(0.079) = 0.158M

Checkpoint

$H_2(g) + I_2(g) \leftrightarrows 2HI(g)$

At 700K, the K_{eq} = 57.0. Calculate the concentrations of $H_2(g)$, $I_2(g)$, $HI(g)$ at equilibrium if the initial concentrations are $[H_2]$ = 0.100M and $[I_2]$ = 0.200M.

Step 1: $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$

	$H_2(g)$	$I_2(g)$	$2HI(g)$
Initial (M)	0.100	0.200	0.00
Change (M)	-x	-x	+2x
Equilibrium (M)	0.100-x	0.200-x	2x

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

$$57.0 = \frac{(2x)^2}{(0.100 - x)(0.200 - x)}$$

$$57.0 = \frac{(2x)^2}{(x^2 - 0.300x + 0.02)}$$

To solve for *x*, use quadratic formula

$$57.0(x^2 - 0.300x + 0.02) = 4x^2$$

$$57.0x^2 - 17.1x + 1.14 = 4x^2$$

$$53.0x^2 - 17.1x + 1.14 = 0$$

$$a = 53.0$$
$$b = -17.1$$
$$c = 1.14$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
$$x = \frac{17.1 \pm \sqrt{(-17.1)^2 - 4(53.0)(1.14)}}{2(53.0)}$$
$$x = \frac{17.1 \pm 7.12}{106}$$
$$x = 0.228 \text{ and } 0.0941$$

Choose 0.0941M:

$[H_2]$ = 0.100 – x = 0.100 – 0.0941 = 0.0059M

$[I_2]$ = 0.200 – x = 0.200 – 0.0941 = 0.1059M

[HI] = 2x = 2(0.0941) = 0.1882M

Approximation with Small K_{eq}

- When K_{eq} is small compared to the initial concentration, the value of the (initial concentration – x) is approximately equal to the initial concentration so you can ignore x
- Divide the smallest initial concentration by the value of K_{eq}:
  - Answer > 500 = ignore x
  - Answer between 100-500 = maybe ignore x
  - Answer < 100 = use quadratic formula

Checkpoint

$N_2(g) + O_2(g) \leftrightarrows 2NO(g)$

The chemist puts 0.085mol of $N_2(g)$ and 0.038mol of $O_2(g)$ in a 1.0L cylinder. At a certain temperature, the value of $K_{eq} = 4.2x10^{-8}$. What is the concentration of NO(g) in the mixture at equilibrium?

Step 1: $N_2(g) + O_2(g) \leftrightarrows 2NO(g)$

Step 1 $\dfrac{\text{Smallest initial concentration}}{K_c} = \dfrac{0.038}{4.2 \times 10^{-8}}$

$= 9.0 \times 10^5$

Because this is well above 500, you can ignore the changes in $[N_2]$ and $[O_2]$.

Step 2

Concentration (mol/L)	$N_{2(g)}$	+	$O_{2(g)}$	$\rightleftharpoons$	$2NO_{(g)}$
Initial	0.085		0.038		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.085 - x \approx 0.085$		$0.038 - x \approx 0.038$		$2x$

Step 3

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$4.2 \times 10^{-8} = \frac{(2x)^2}{0.085 \times 0.038}$$

$$= \frac{4x^2}{0.003\,23}$$

$$x = \sqrt{3.39 \times 10^{-11}}$$

$$= 5.82 \times 10^{-6}$$

Step 4 $[NO] = 2x$

Therefore, the concentration of $NO_{(g)}$ at equilibrium is 1.2×10^{-5} mol/L.

Reaction Quotient Q

- K_{eq} is the constant at equilibrium
- Q is the constant at any point in time, not just at equilibrium
  - Q lets us predict the direction of the reaction by comparing Q and K_{eq}

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

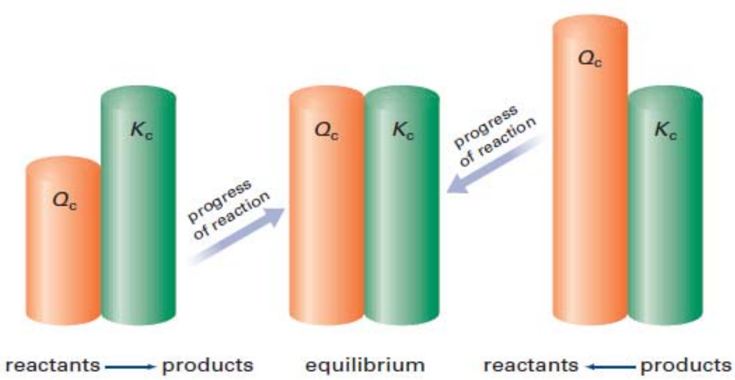


Figure 7.8 This diagram shows how Q_c and K_c determine reaction direction. When $Q_c < K_c$, the system attains equilibrium by moving to the right, favouring products. When $Q_c = K_c$, the system is at equilibrium. When $Q_c > K_c$, the system attains equilibrium by moving to the left, favouring reactants.

- If $Q < K_{eq}$, net reaction goes from reactants to products
- If $Q = K_{eq}$, no net reaction, in equilibrium
- If $Q > K_{eq}$, net reaction goes from products to reactants

Checkpoint

$2COF_2(g) \leftrightarrows CO_2(g) + CF_4(g)$

The K_{eq} for this reaction is 2. If a 1L reaction container holds 1mol each of CO_2 and CF_4 and 0.5mol of COF_2, how will the reaction proceed?

Le Chatelier's Principle

- If stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress
- Factors:
  - Concentration of reactants or products
  - Pressure and volume
  - Temperature

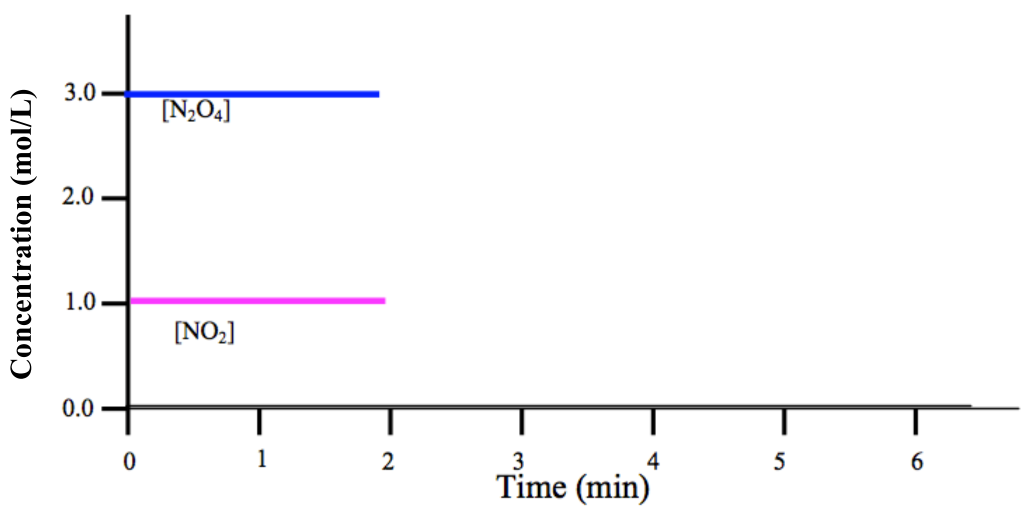
Changes in Concentration

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ K_c=0.291 at 700K

- If we increase $[N_2]$, Le Chatelier's Principle tells us that the reaction will relieve the excess by converting the N_2 into NH_3
- If we decrease $[N_2]$, the reaction will go from right to left to compensate for the decrease

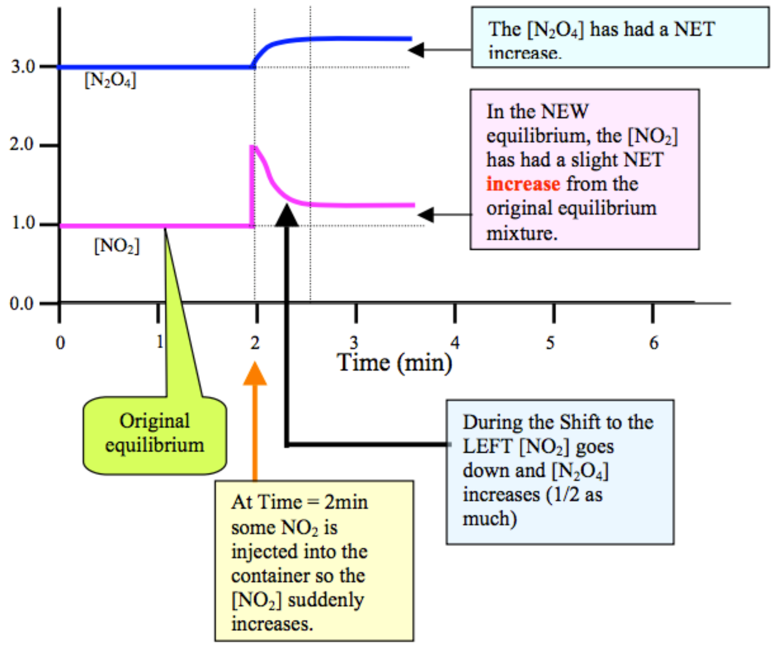
$N_2O_4(g) + heat \leftrightarrows 2NO_2(g)$

$[N_2O_4]$ is 3.0M and $[NO_2]$ is 1.0M



$N_2O_4(g)$ + heat ⇆ $2NO_2(g)$

Increase $[NO_2]$ to 2.0M at 2min



Common Ion Effect

$Mg(OH)_2(s) \leftrightarrows Mg^{2+}(aq) + 2OH^-(aq)$

- If we added NaOH to this solution, it would dissociate into $Na^+(aq)$ and $OH^-(aq)$
- Addition of NaOH caused an increase in OH^-, which means the concentration of the products has increased
- System will move towards the left to compensate

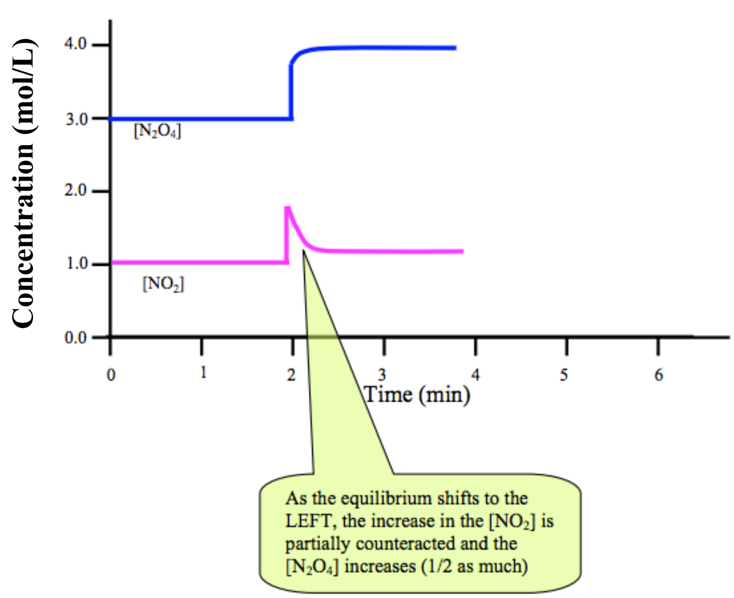
Change of Volume and Pressure

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$

- If we decrease the volume, we increase the pressure = towards the direction that decreases the number of moles of gas
- If we increase the volume, we decrease the pressure = towards the direction that increases the number of moles of gas
- If you increase the pressure by adding an inert gas, equilibrium remains unchanged

$N_2O_4(g) + heat \leftrightarrows 2NO_2(g)$

Decrease Volume



Change of Temperature

- Heat can be treated like a reactant or a product

Exothermic (ΔH<0)

Reactants ⇆ Products + Heat

- If you increase the temperature, the system will move towards the reactants

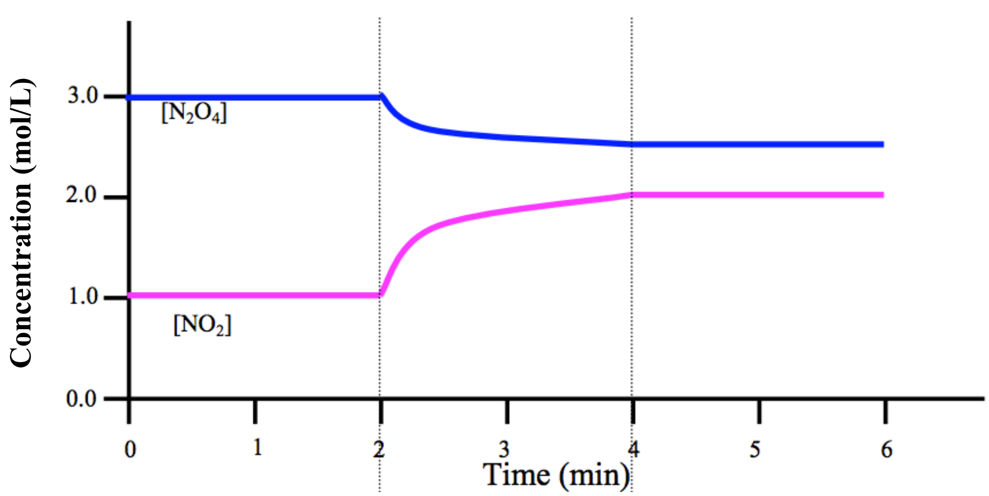
Endothermic (ΔH>0)

Reactants + Heat ⇆ Products

- If you increase the temperature, the system will move towards the products

$N_2O_4(g)$ + heat ⇆ $2NO_2(g)$

Increase temperature



Adding a Catalyst

- Recall that the catalyst lowers the activation energy thereby increasing the rate of reaction
- Because the rates of the forward and reverse reaction increase by the same factor, adding a catalyst has no effect on the equilibrium
- A catalyst only affects the time it takes to achieve equilibrium

Checkpoint

$PCl_5(g) \leftrightarrows PCl_3(g) + Cl_2(g)$ $\Delta H = 56kJ$

For the above reaction, in which direction does the equilibrium shift as a result of each change?

a) Adding $PCl_5(g)$
b) Removing $Cl_2(g)$
c) Decreasing the temperature
d) Increasing the pressure by adding helium gas
e) Using a catalyst

Checkpoint

$[Co(H_2O)_6]^{2+}(aq)$(**pink**) + $4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq)$(**blue**) + $6H_2O(l)$

For the above endothermic reaction, graph the equilibrium shift as a result of the following changes:

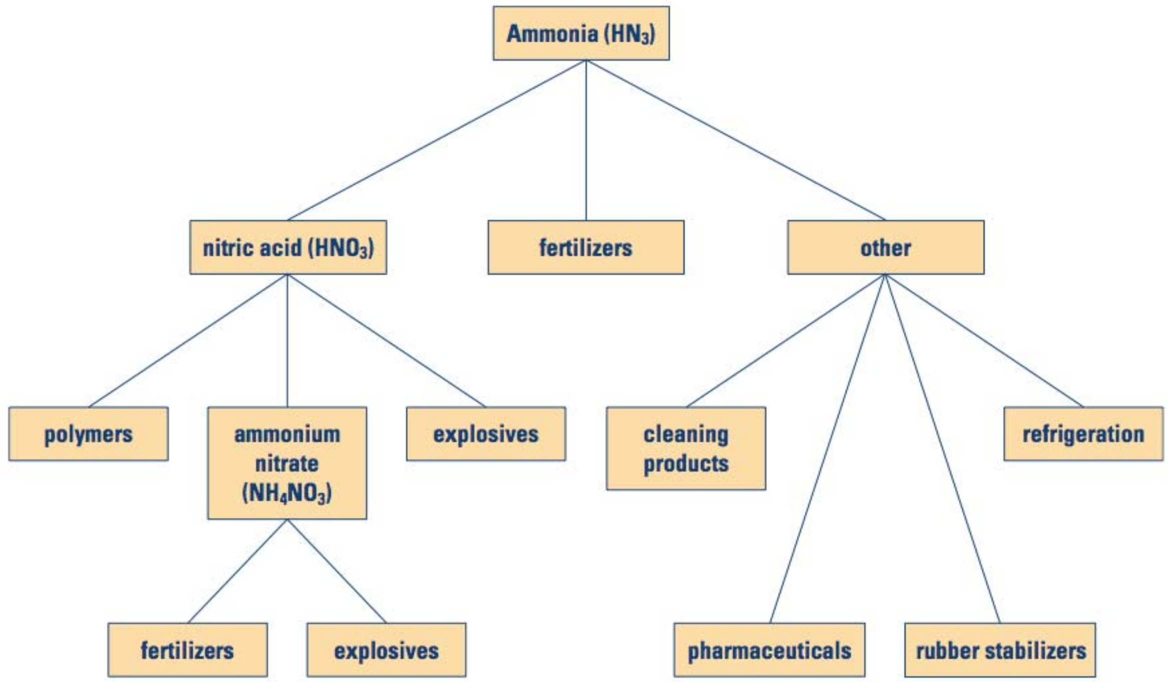
a) Adding $H_2O(l)$
b) Adding $HCl(aq)$
c) Adding $Pb(NO_3)_2$
d) Ice Bath
e) Heat Bath
f) Catalyst

Manufacturing Ammonia

- Global production of ammonia is 100 million tonnes
  - 80% used to make fertilizers
- Originally derived from bird droppings in Peru to be used as fertilizer; scarce and expensive
- Fritz Haber experimented with the direct synthesis of ammonia

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

- As the ammonia is created under high pressure, it is removed from the reaction vessel to shift the equilibrium towards the production of more ammonia
- Haber also chose an iron catalyst that would work well for higher temperatures
- Carl Bosch designed the high pressure plant to allow for the synthesis of ammonia under high pressure
- Haber-Bosch process is used to manufacture almost all ammonia produced in the world


Ammonia (HN_3)
nitric acid (HNO_3)
fertilizers
other
polymers
ammonium nitrate (NH_4NO_3)
explosives
cleaning products
refrigeration
fertilizers
explosives
pharmaceuticals
rubber stabilizers