LECTURE 1

Why study chemical reaction engineering?

What does the term even mean?

This year marks the 100th anniversary of the start of World War I. → specific to 2014

The birth of modern chemical engineering as we know it started a little before but was led by one of the major figures in the War.

Any guesses who this figure is?

FRITZ HABER

His biography is called Fritz Haber: Chemist, Nobel Laureate, German, Jew.

Haber is known as the Father of Chemical Warfare. He led the development of deadly gases for trench warfare, including weaponised chlorine.

Why am I telling you this?

Because Haber can very well be called as one of the pioneers of chemical engineering.

He formed a formidable tag-team with Carl Bosch, a German chemical engineer & revolutionised the production of food.

Their process is called the Haber-Bosch process.

It was devised in 1909.

It led to Nobel Prizes to Haber & Bosch.

It is the poster child of chemical reaction engineering.

It marked the beginning of chemical engineering emerging as a profession that could transform the world we live in.

What is the Haber-Bosch process?

It is a process for production of synthetic ammonia.

Ammonia is then used to produce fertilizers, explosives & chemical feedstocks.

Synthetic? How was ammonia produced before?

From sodium nitrate: Chile was the major & almost unique producer.

Before Haber-Bosch

2.5 million tons of $NaNO_3$
60,000 wokers
$45/ton

$112.5 million

After Haber-Bosch

800,000 tons
14,000 wokers
$19/ton

* + Angry Chileans

$15.2 million
↳ $0 today

Haber-Bosch Process:

* 500 million tons of artificial fertilizer produced by it
* Uses 1% of world's energy supply
* Feeds half of world's population

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92.1\ kJ$$

$N_2 + 3H_2$: 4 moles; $\rightleftharpoons$: equilibrium; $2NH_3$: 2 moles; $\Delta H = -92.1\ kJ$: exothermic

equilibrium → Le Chatelier's principle

Let us scale-up the process.
What does Le Chatelier's principle tell us?

To improve yield:

① increase pressure (raises the 'driving force')

② decrease temperature

But this is easier said than done, why?

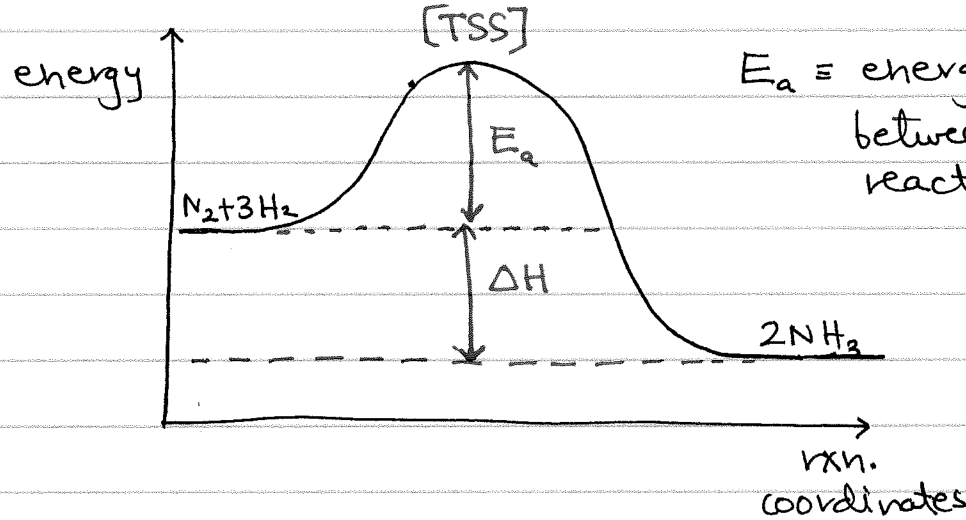
① Increasing pressure ⇒ makes process more dangerous

② Lowering the temperature:

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

- k → rate constant (units depend on order of rxn.)
- A → frequency factor (same units as k)
- E_a → activation energy (J/mol)
- T → temperature (in K)
- R → universal gas constant ($\simeq 8.314 \frac{J}{mol \cdot K}$)

Recall from physical chemistry:



E_a = energy difference between TSS & reactants

E_a & ΔH are of a similar order of magnitude.

For this reaction, let us assume $E_a = 50 \frac{kJ}{mol}$ & $A = 10^9\ s^{-1}$ (usually TSS)

At 30°C i.e. 303 K:

$$k_1 = A \exp\left(\frac{-50{,}000}{8.314 \times 303}\right)$$

$$\therefore k_1 = 2.3994\ s^{-1}$$

At 20°C i.e. 293 K

$$k_2 = 1.2188\ s^{-1}$$ (~50% reduction)

What happens to the rate constant as temperature is lowered?

It drops!

Therefore, the reaction takes longer to finish. It has a higher yield at lower temperature. But its productivity is lower.

③ The process is tough to control

From the ideal gas law:

$$PV = nRT$$

↑ each of these will change over the duration of the reaction

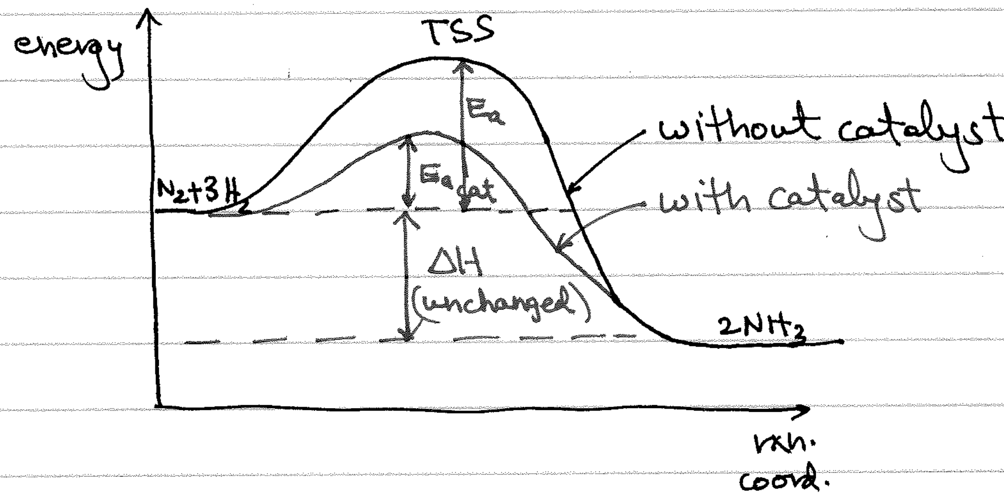
i.e. $$dP = \frac{R}{V}\left(n\,dT + T\,dn\right)$$ ← not fun!

So what did Haber & Bosch do?

They synthesized a special catalyst.

What does a catalyst do?

* It accelerates the process without taking part in the reaction.



The catalyst facilitates (& stabilises) formation of the TSS, thereby reducing the E_a.

Haber & Bosch developed an iron-based catalyst.

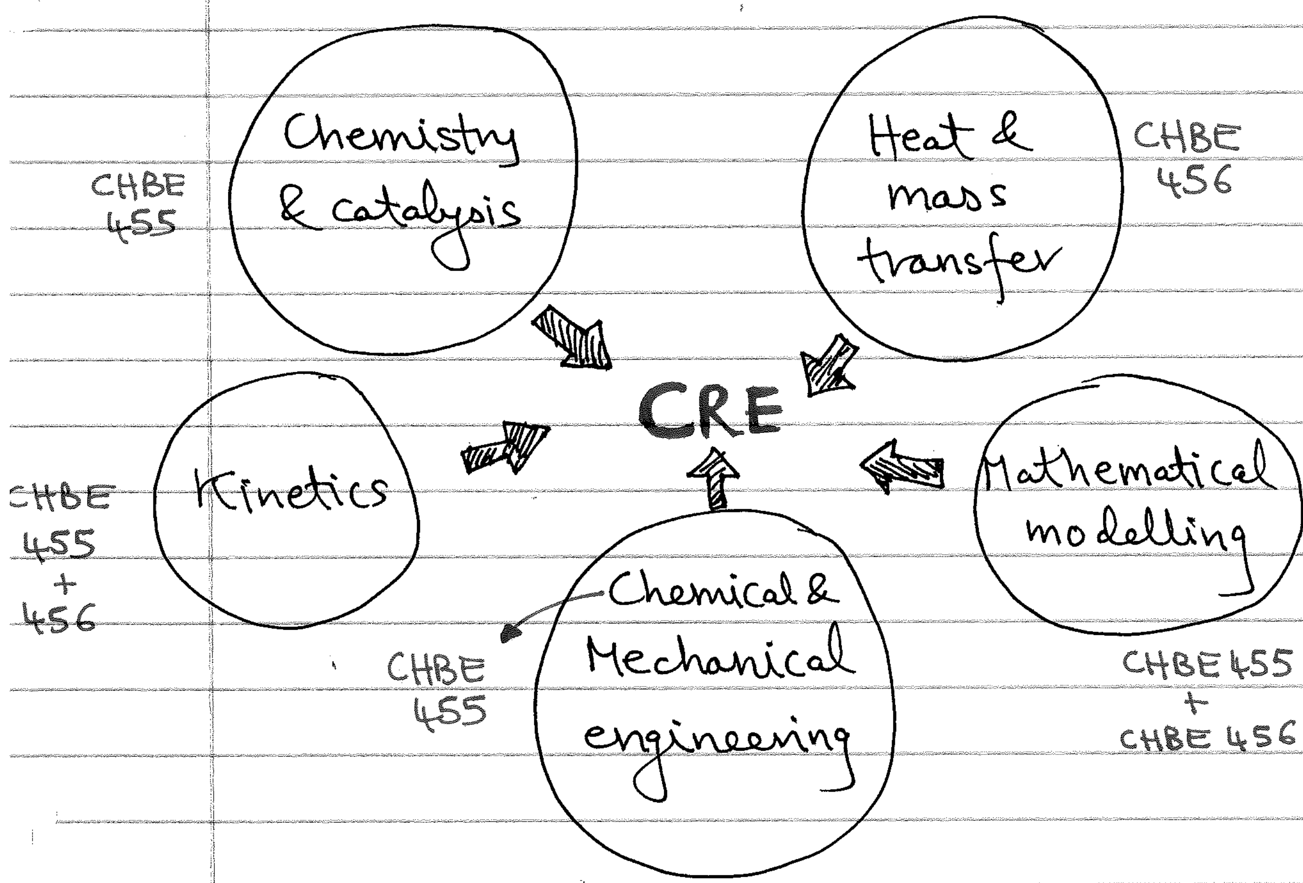
They also optimised the process.

How?

Using their understanding of kinetics, equilibrium, transport phenomena & reactor design

What does the final process look like?

* 200 atm pressure
* ~300°C
* The gases pass through a catalyst bed
* There are ~4 beds & the gases are cooled between passes.
* Overall conversion is 97%
* The vessel is about 2-3 storeys high
* It is made of steel



Steps in Haber-Bosch:

$H_2 \rightleftharpoons H_2^*$

gas adsorbed

$H_2^* \rightleftharpoons 2H^*$

$N_2 \rightleftharpoons N_2^*$

$N_2 \rightleftharpoons 2N^*$ rate-limiting step

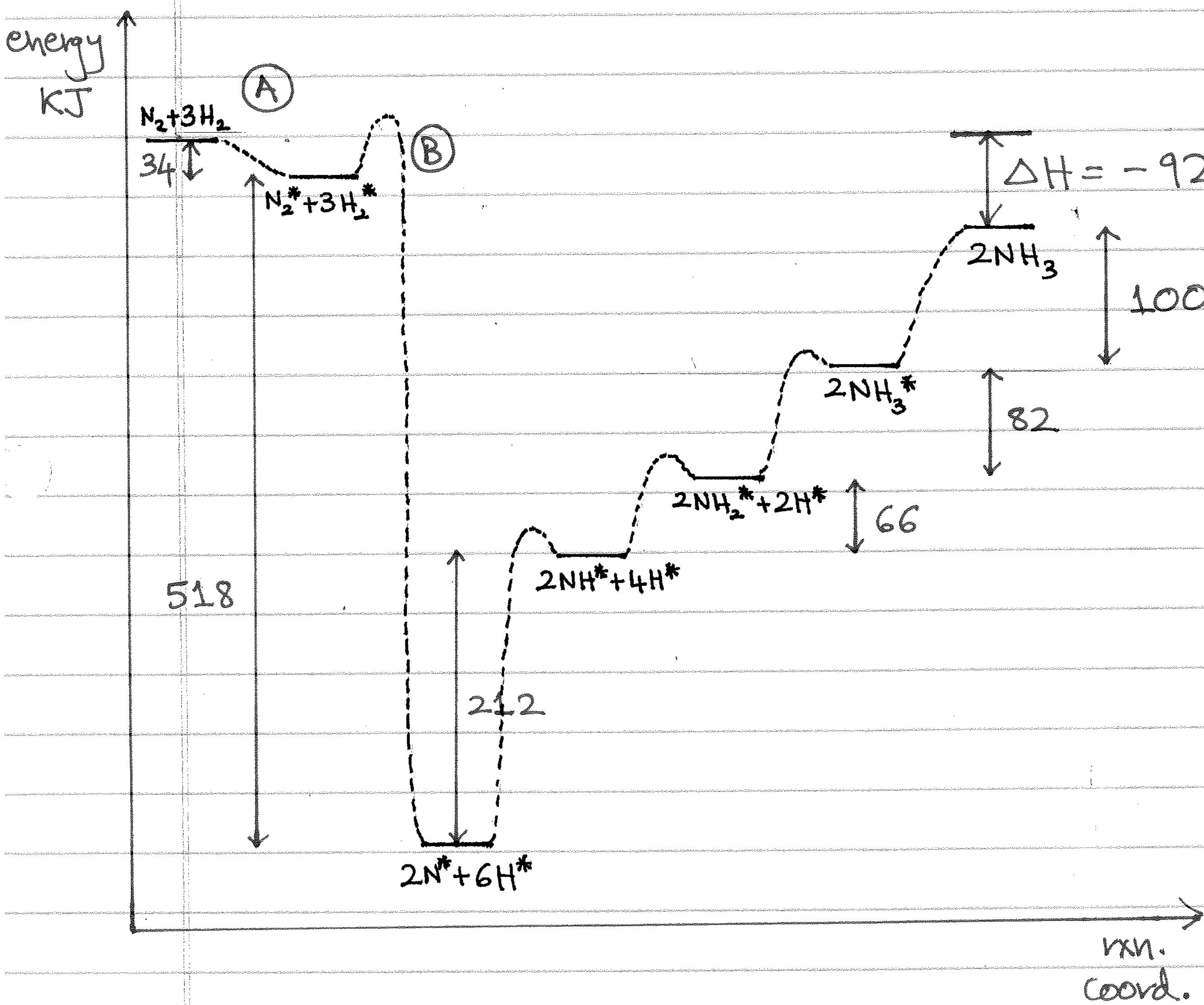
$N^* + H^* \rightleftharpoons NH^*$

$NH^* + H^* \rightleftharpoons NH_2^*$

$NH_2^* + H^* \rightleftharpoons NH_3^*$

$NH_3^* \rightleftharpoons NH_3$

Potential Energy Diagram for Haber–Bosch Process:



Self-study questions:

- Why are the curves for (A) & (B) shaped differently?
- Can you identify the rate-limiting step?

The algorithm