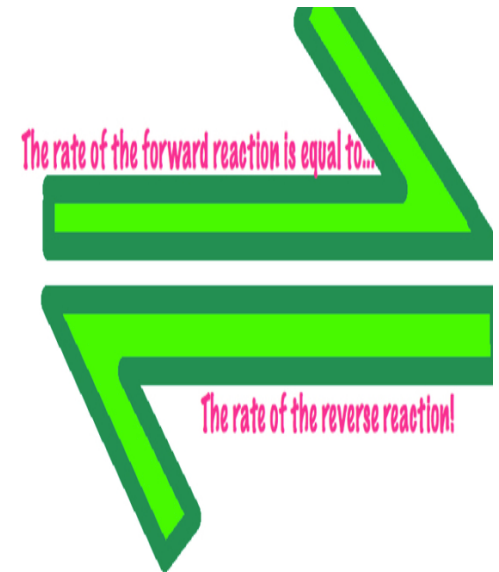


Topic 7.1

Equilibrium reactions in chemistry

- Many important chemical reactions are reversible and exist in equilibrium.
- Equilibrium is when the forward and reverse reactions are occurring at the same time. The concentration of product and reactant won't change.
 - Useful for industries to understand to maximize yield of desired products
- Dynamic equilibrium is when the concentration for products and reactants does not change but there is still products changing into reactants and vice versa at a constant rate



Heterogeneous equilibrium and solubility

- Consider when you have a closed system and a solid, such as NaCl, is added into water.
 - NaCl will begin to dissolve into the water. The amount of NaCl that is aqueous will increase. (Not equilibrium)
 - Eventually, NaCl will become saturated in the aqueous solution. At this point the concentration of NaCl dissolving will be equal to the concentration of NaCl coming out of solution. (equilibrium)
 - At equilibrium, the saturated solution will exist and NaCl solid will exist

Chemical systems

- Many reactions never go to completion
- The relative rates of forward and reverse reaction rates depend on both physical and chemical conditions
 - Physical conditions include temperature and pressure
 - Chemical conditions include a change in the concentration of reactants and products
 - Catalysts

At equilibrium

- There is no change in the concentration of products and reactants
- The rate of the forward and back reactions are the same
- There is no change in the macroscopic properties (large) such as color or density
- The equilibrium is dynamic. Even though the concentrations of the reactants and products don't change the forward and reverse reaction take place still.
- Any changes to the conditions around the experiment can change the equilibrium demonstrating that it is dynamic.
- Must be closed
- All products and reactants will be present

Equilibrium Constant

- If all the products and reactants are in the same phase then the following equation can be used to figure out its equilibrium constant.
 - $aA + bB \rightleftharpoons cC + dD$ The arrow means equilibrium has been reached
 - $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ where K_c is the equilibrium constant at a particular temperature
 - K_p can be used for gases to represent the equilibrium constant for a particular pressure.
 - K_c can tell us which part of the equation is favored at a particular temperature. If K_c is bigger than one then the products are favored and if K_c is less than one the reactants are favored.

Combining/changing equilibrium constants

- K_c reverse-

- Assume $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ then $K_{c\ reverse} = \frac{[A]^a[B]^b}{[C]^c[D]^d}$ thus we can say

$$K_{c\ reverse} = \frac{1}{K_c} \text{ or } K_c^{-1}$$

Combining/changing equilibrium constants

- $K_c \text{ double}^-$

- Assume $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ then $K_c \text{ double} = \frac{[C]^{2c}[D]^{2d}}{[A]^{2a}[B]^{2b}} = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)^2$ thus we can say

$$K_c \text{ double} = K_c^2$$

Combining/changing equilibrium constants

- K_c halved⁻

- Assume $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ then $K_{c \text{ halved}} = \frac{[C]^{1/2c} [D]^{1/2d}}{[A]^{1/2a} [B]^{1/2b}} = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)^{\frac{1}{2}}$ thus we can say

$$K_{c \text{ halved}} = \sqrt{K_c}$$

Combining/changing equilibrium constants

- K_{c1+2}
- Assume reaction one is $aA \rightleftharpoons cC$ and reaction 2 is $bB \rightleftharpoons dD$ then
- $K_{c1} = \frac{[C]^c}{[A]^a}$ and $K_{c2} = \frac{[D]^d}{[B]^b}$
- Reaction 1+2 is $aA + bB \rightleftharpoons cC + dD$
- Then $K_{c1+2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ so we can say that $K_{c1+2} = K_{c1} * K_{c2}$

Changing experimental conditions

- Le Chatelier's principle is used for predicting the effect that changing an experimental condition will have on the equilibrium positions.
- The principle states: *If a change is made to a system that is in equilibrium the balance between the forward and the reverse reactions will shift to offset this change and return the system to equilibrium.*

Changing experimental conditions

- Adding/removing more product or reactant:
 - If more product is added to the system the system wants to return to equilibrium. So the system will change the product to reactant and shift the equilibrium to the left (reactants). The equilibrium constant is unchanged.
 - If product is removed as it is made then the system also becomes stressed. The system will make more product to remove the stress and shift the equilibrium to the right (products). The equilibrium constant is unchanged.
 - Similar things can be said if you were removing/adding the reactants.



Changing experimental conditions

- Changing pressure
 - Only effects reactions that have gases involved.
 - Increasing the pressure shifts the reactions away from the side with the most gas molecules to reduce the pressure to its equilibrium state.
 - This does not change the value of the equilibrium constant.

Changing experimental conditions

- Temperature change:
 - If a reaction is exothermic in the forward direction then it is endothermic in the reverse direction and vice versa.
 - If the temperature decreases then the equilibrium will shift towards the direction of the exothermic reaction to combat the temperature change and the equilibrium will shift towards the reaction that is endothermic if there is a temperature increase.
 - The equilibrium constant will change because the temperature will change.

Changing experimental conditions

- Addition of a catalyst- Adding a catalyst will not shift equilibrium because it changes both the forward and reverse reactions activation energies. This will not change the equilibrium constant either.

Reaction Quotient

- $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ when equilibrium has not been reached.
- If Q is greater than K_c then there are more products than should be present and the reaction is moving towards the reactants
- If Q is less than K_c then there are more reactants than should be present and the reaction is moving towards the products
- If $Q = K_c$ then equilibrium has been reached.

The Haber Process (Nature of science)



- This reaction makes ammonia out of hydrogen and nitrogen.
- The nitrogen comes from the air (78% N).
- Haber also used this process to make chemical war techniques for the Nazi during WWII
- Creates Fertilizer
- Used as an explosive in mining

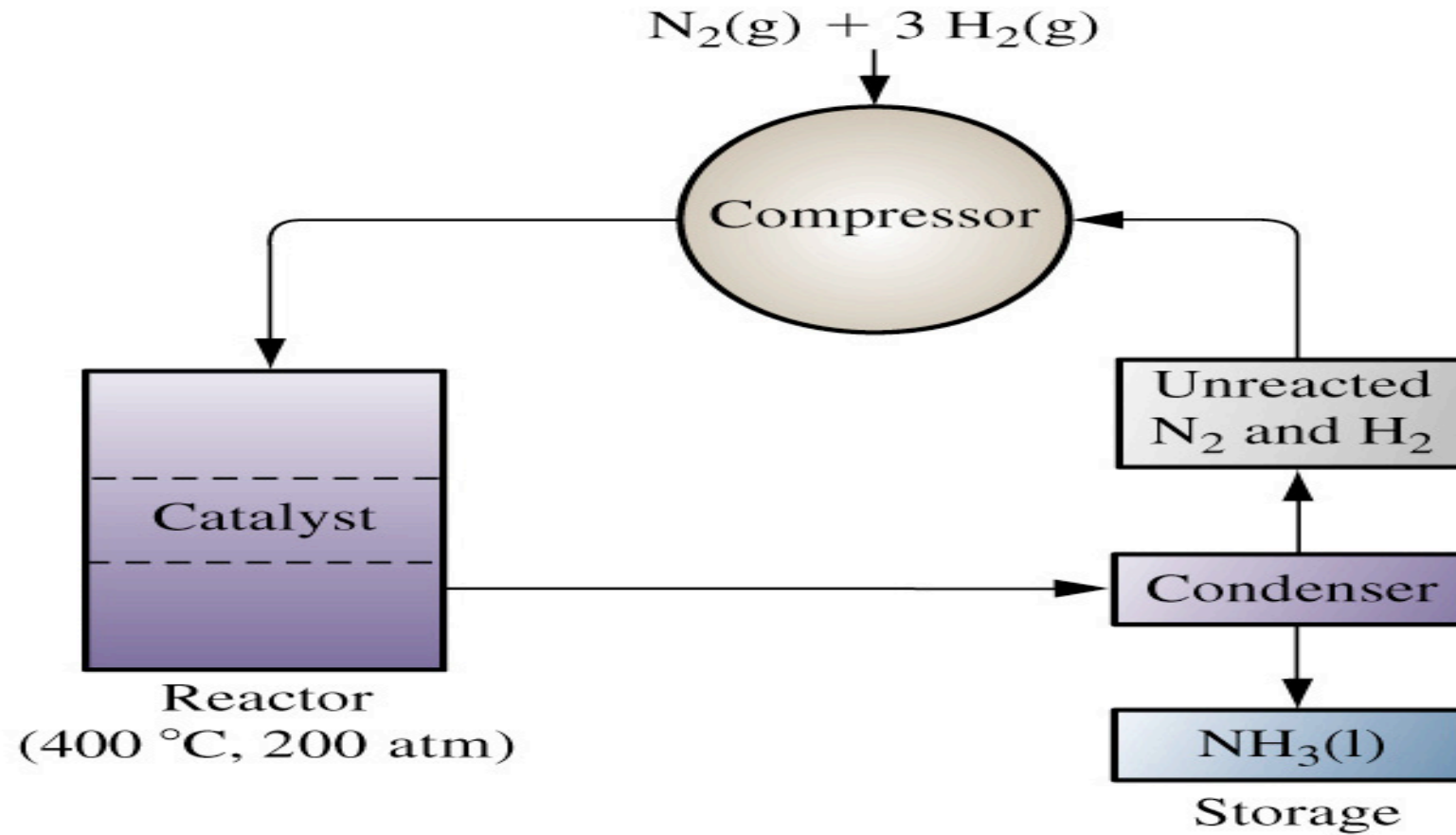
The Haber Process

- The Haber process is a **REVERSIBLE** reaction



A reversible reaction is one where the products of the reaction can themselves react to produce the original reactants.

The Haber Process



The Haber Process

- You need to **LEARN** the industrial conditions this reaction occurs in off by heart – this is a favourite exam question!!!

- Industrial conditions:

PRESSURE: 200 atmospheres

TEMPERATURE: 500⁰C

CATALYST: Iron

From: <http://hepq.pbworks.com/f/The+Haber+Process.ppt>

The Haber

Key facts

1. H and N are mixed in a 3:1 ratio
2. Because the reaction is reversible not all the nitrogen and hydrogen will convert to ammonia.
3. The ammonia forms as a gas but cools and liquefies in the condenser
4. The H and N which do not react are passed through the system again so they are not wasted.

From: <http://hepq.pbworks.com/f/The+Haber+Process.ppt>

The Contact Process (Nature of science)

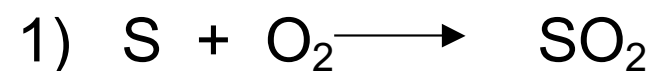
from: https://www.chem.tamu.edu/class/majors/chem470/Sulfuric_Acid-2008.PPT

- One of the oldest industrially applied processes. Discovered by a Persian alchemist in the tenth century.
- Saltpeter and sulfur were mixed in a glass container and burned in a moist atmosphere. Acid was collected from the condensed vapors.
- In England, 1746, the lead chamber reactor was invented. This invention allowed for higher production rates (<78%).
- In England, 1831, a patent was filed that described the oxidation of sulfur dioxide over a platinum catalyst, the Contact Process. This new process increased yields of reaction from 70 to above 95%.
- In 1913, BASF was granted a patent for the use of vanadium pentoxide as a catalyst for the Contact Process
- By the 1930's, vanadium pentoxide was becoming the dominate catalyst used because of insensitivities to poisons and lower cost.
- In 1960 a patent application was filed by Bayer using the so called double-catalyst process (double absorption).

The Contact Process (Nature of science)

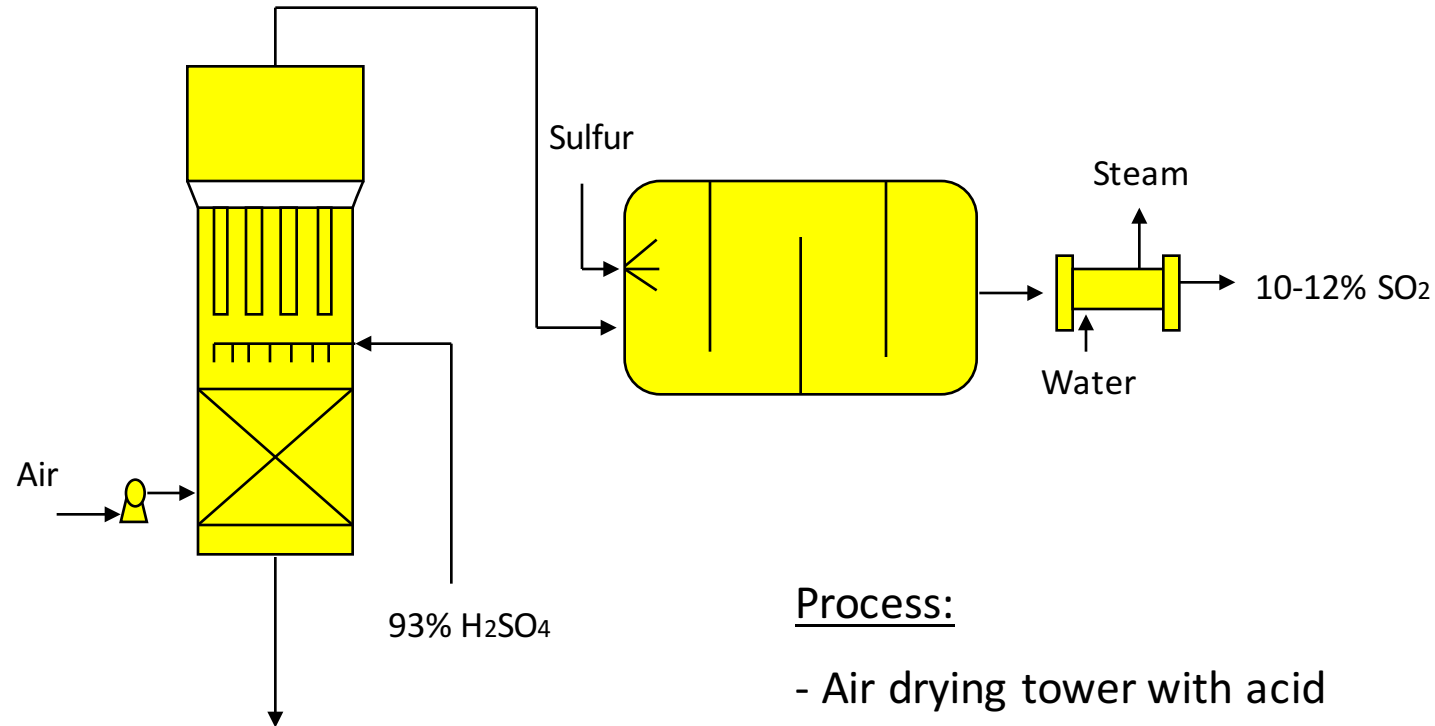
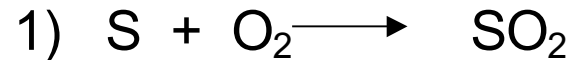
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Three Step Process



The Contact Process (Nature of science)

from: https://www.chem.tamu.edu/class/majors/chem470/Sulfuric_Acid-2008.PPT



Primary Generation of SO₂

- 79% Combustion of Sulfur
- 9% Recovery from Metallurgic Processes
- 5% Regeneration of Spent Acids

Process:

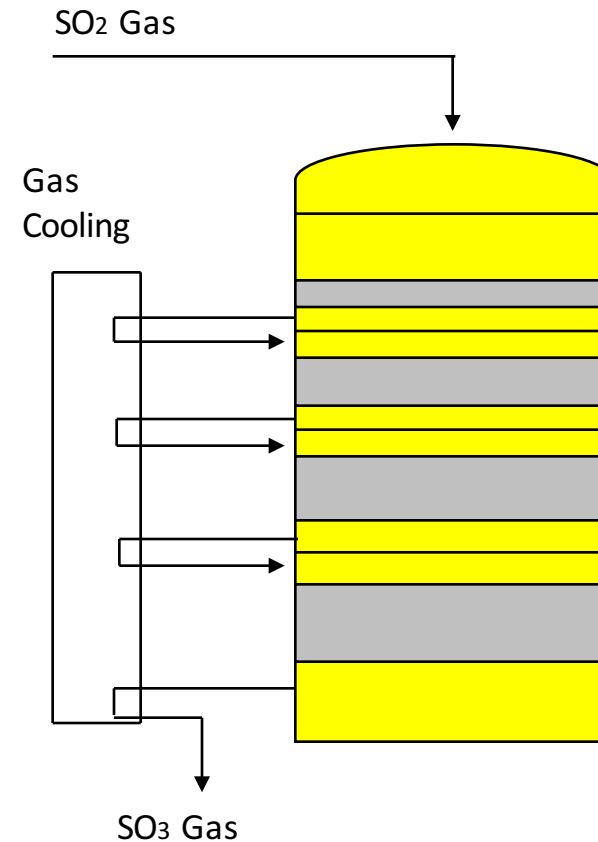
- Air drying tower with acid
- Sulfur is injected into burner
- Reaction Temperature 2000°F
- Exothermic reaction must be cooled
- Steam recovered

The Contact Process (Nature of science)

from: https://www.chem.tamu.edu/class/majors/chem470/Sulfuric_Acid-2008.PPT

Contact Process:

- Vanadium pentoxide catalyst
- Exothermic Reaction
- Multiple Steps with cooling in between
- Double absorption
- Heat integration



The Contact Process (Nature of science)

from: https://www.chem.tamu.edu/class/majors/chem470/Sulfuric_Acid-2008.PPT

- Because of the large effect temperature plays on the reaction, multiple catalyst layers are used, with cooling between each step.
- Additionally, as the partial pressure of SO_3 increases, further reaction is limited.
 - This is overcome by removing the SO_3 after the third stage to drive the reaction to completion.

