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Manufacture of Nitric Acid, Physico-Chemical Principles (Ostwald's Process), Uses of nitric acid

Manufacture of Nitric Acid

Like sulphuric acid, nitric acid is also an important product of chemical industry. It is used in synthetic fibers, dyestuffs, explosives, plastics, drugs it is also used in manufacture of nitrogen fertilizers like ammonium nitrate and mixed fertilizers like nitro phosphate.

Manufacture of nitric acid by Ostwald's Process (Ammonia Oxidation Method)

Raw Materials: Anhydrous (dry) ammonia, air, water platinum-rhodium

Chemical Reactions

Ostwald's process involves following steps.

(1) Oxidation of ammonia to nitric oxide with air or oxygen in presence of Pt-Rh catalyst

$$4\ NH_3 + 5O_2 \longrightarrow 4NO + 6\ H_20 + 950\ kJ$$

(ii) Oxidation of nitric oxide to nitrogen dioxide

$$2\ NO + O_2 \longrightarrow 2\ NO_2 + 114KJ$$

(iii) Absorption of NO: by water.

$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO \quad +134\ KJ$$

The process of manufacture of nitric acid can be described in the following steps

Ammonia, prepared by Haber's process is scrubbed with sodium hydroxide and then freed from water by refrigeration. Ammonia is purified The purified ammonia is vaporized in a continuous steam evaporator Air is compressed to 6.8 atmospheres, filtered and preheated to about 300C by passing through a heat exchangers. Ammonia is mixed with purified and preheated air in proportion 1:10 by volume The mixture of gases (NH3, air) is compressed to a pressure of 100 psi. &

Reaction in a Reactor (Converter)

The reactor contains Pt-Rh catalyst gauze and it is fitted on a horizontal grid made of nickel-chromium-steel. There is an electrical heating arrangement for starting the reaction.

The compressed mixture of gases (NH_3, air) is passed over Pt-Rh wire gauze catalyst in a reactor which is heated to 750°C. Here ammonia is oxidized in a reactor to nitric oxide

$4\ NH_3 + 5O_2 \longrightarrow 4NO + 6\ H_2 0 + 950\ kJ$

Once the temperature is reached to about 800°C, afterwards the temperature is maintained by the beat of the reaction itself (ie, due to exothermic process)

The hot gaseous mixture of NO, N. O_2 and steam coming out of the converter is passed through a heat exchanger to lower down the temperature of the gases

Reaction in the Absorber

The cooled gas is introduced into a stainless steel absorption tower and cooked externally with water. Here more air is added for further oxidation of NO to NO_2

$2\ NO + O_2 \longrightarrow 2\ NO_2 + 114KJ$

The gases are further cooled in 'S' shaped condensers with cold water. The NO, formed reacts with water and gives dilute nitric acid.

3NO2 +H2O ⟶ 2 HNO3 +NO +134 KJ

Waste gases are released from the top of the tower and nitric acid is obtained at the bottom. The conversion of ammonia to nitric acid is about 93%

Physico-Chemical Principles (Ostwald's Process)

There are three important steps involved in the Ostwald's process for manufacture of nitric acid.

(i) Oxidation of NH_3 to NO
(ii) Oxidation of NO to NO_2
(iii) Absorption of NO_2 in water to form HNO_3

Principles Involved In the Oxidation of NH_3 to NO The most important step in the manufacture of nitric acid by Ostwald's process is the catalytic oxidation of NH3 to NO.

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O + 950kJ$$

This reaction is reversible and forward reaction is exothermic. Here 9 volumes of the reactants give 10 volumes of the products. Thus there is little increase in the volume when NO is formed

Effect of Temperature:

Since the reaction is exothermic, it is expected that low temperature, will favors this reaction. However, at low temperature, the rate of reaction is slow. So an optimum temperature of about 750°C is kept when pressure is 6.8 atmospheres At higher temperature, there is a tendency of (1) ammonia to get oxidised to N2 and decomposition of NO2 Thus, the efficiency of the process is decreased. The catalyst is only initially electrically heated to about 800°C and then the reaction continues on its own maintaining that temperature.

Effect of Pressure - The forward reaction proceeds with little increase in volume and backward reaction proceeds with little decrease in volume. If we increase the pressure, equilibrium will shift to a small extent to the left decreasing the yield of NO. But there is some other advantage in increasing the pressure. If we increase the pressure, the space velocity (volume of the leaving gas corrected to N.T.P. conditions which passes over one cubic foot of catalyst per second) increases, hence larger volume of the gas is converted by the same volume of catalyst. Thus a small proportion of catalyst is sufficient. The increase of pressure shifts the equilibrium to the right, hence larger amount of nitric acid is formed at high pressure. The pressure applied, in practice is 6.3 atmospheres

Effect of Catalyst: it is found that when a catalyst is taken in the form of age, it is effective. A multilayered catalyst, made of 10% Rh and 90% Pt taken used as catalyst. The conversion of NH_3 by mixed with preheated air (At 300°C) takes place through this catalyst at a temperature of 750^0 C The yield of NO is about 94 to 95%

Effect of Proportion of Gases (NH_3 and air) :

Excess of oxygen should be taken because some oxygen is also required to convert NO to NO, Generally, the mixture consists 10% NH_3 and 90% air by volume. If the proportion of ammonia in the mixture exceeds 10%, there is a danger of explosion because the reaction takes place under high pressure (68 atmospheres) Similarly, many side reactions may occurs that reduce the yield of NO and more NH_3 is wasted.

Rate of Flow of Gases In the reactor all ammonia should get oxidized at once, otherwise a second reaction between unused ammonia and nitric oxide produced in the main rection may take place

$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$

So the gases should not remain in contact with the catalyst for a long time. The rate of flow of gases should be high. For Rh-Pt catalyst at 750°C, If the contact is longer, NO is decomposed to N_2 and O_2

Principles Involved In Oxidation of NO to NO_2:

$2\,NO + O_2 \rightleftharpoons 2\,NO_2 + 114KJ$

This reaction is also reversible. The forward reaction is exothermic and there is decrease in volume when NO_2 is formed. According to Le Ch atelier's principle, high pressure and low temperature is favorable for oxidation of NO to NO_2. This conversion of NO to NO_2 takes place at 150°C and 6.8 atmospheres pressure. Since the reaction is slow, more contact time is necessary for oxidation.

(iii) Principles Involved In Absorption of NO_2 In Water

$3NO_2 + H_2O \rightleftharpoons 2\,HNO_3 + NO + 134\ KJ$

Absorption being a slow process, more space is required for it. Absorption of NO_2 by water under controlled process gives nitric acid. The forward reaction is exothermic and hence the rate of reaction can be increased by cooling the gases to 40°C to 50°C and by employing counter current graded strengths of acid for absorption. The nitric acid produced in Ostwald's process is about 61 to 65% in strength.

The favourable conditions for the better yield of nitric acid are

Temperature: 750 C for the conversion of NH_3 to NO

150°C for the conversion of NO to NO_2

Pressure: 6.8 atmospheres

Catalyst :10% Rh-90% Pt

Proportion of Gases: Ammonia: oxygen 10:90%.

Uses of nitric acid

The important uses of nitric acid are as follows:

1) Nitric acid plays a significant role in the manufacture of various products such as Explosives like trinitrotoluene (T. N. T.), gun cotton etc. Fertilizers such as calcium nitrate, ammonium nitrate etc. Nitrate salts such as calcium nitrate, silver nitrate, ammonium nitrate. • Dyes, perfumes, drugs etc, from coal tar products.

2) It is used in the purification of silver, gold, platinum etc.

3) Nitric acid is used in etching designs on copper, brass, bronze ware

4) It is used to prepare "aqua regia" to dissolve the noble elements.

5) It is used as a laboratory reagent.

References: According to the new revised syllabus of Savitribai Phule Pune University from June 2021, Text book of Industrial chemistry for T.Y. B.Sc. course (CH- 505), Sem-V Manali Publication, Nirali Publication and google images