SULPHURIC ACID

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Sulphuric acid (H_2SO_4)

It is called 'oil of vitriol' because in early days it has been prepared from ferrous sulphate crystals (green vitriol) and has an oily appearance. Because of its large applications in industries, it is also known as the ‘King of chemicals’.

Manufacture Of Sulphuric acid by contact Process.

Principle:

1. Production of Sulphur dioxide

2. Oxidation of Sulphur dioxide

3. Conversion of SO_3 into H_2SO_4

1. Production of Sulphur dioxide - It is carried out by powdered sulphur or roasting iron pyrite ore.

$S_8 + 8O_2 \rightarrow 8SO_2$

$4\ FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

2. Oxidation of Sulphur dioxide

Sulphur dioxide is oxidized to sulphur trioxide in the presence of catalyst vanadium pentaoxide (V_2O_5).

$2SO_2 + O_2 \leftrightarrow 2SO_3 + 196.0$ KJ (In presence of V_2O_5)

This step is the key step in the manufacture of H_2SO_4. By applying Lechatelier's principle, the following conditions can be worked out for the better yield of SO_3 :

i) Temperature - As the reaction is exothermic, a low temperature favours the forward reaction.

Optimum temperature is approximately 425˚C.

ii) Pressure - A high pressure favours the process (2 atm.)

iii) Catalyst - The catalyst employed is V_2O_5.

iv) Purity of gases - To prevent poisoning of catalyst the gases must be free from impurities.

v) Excess of O_2 - To obtain better yield of SO_3, excess and pure oxygen is used.

3. Conversion of SO_3 into H_2SO_4

SO_3 is absorbed in conc.H_2SO_4 to get oleum.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)

Oleum may then be diluted with calculated quantity of water to get $H_2S_2O_7$ of desired concentration.

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

The flow sheet of the plant used for manufacture of H_2SO_4 is as shown in figure:

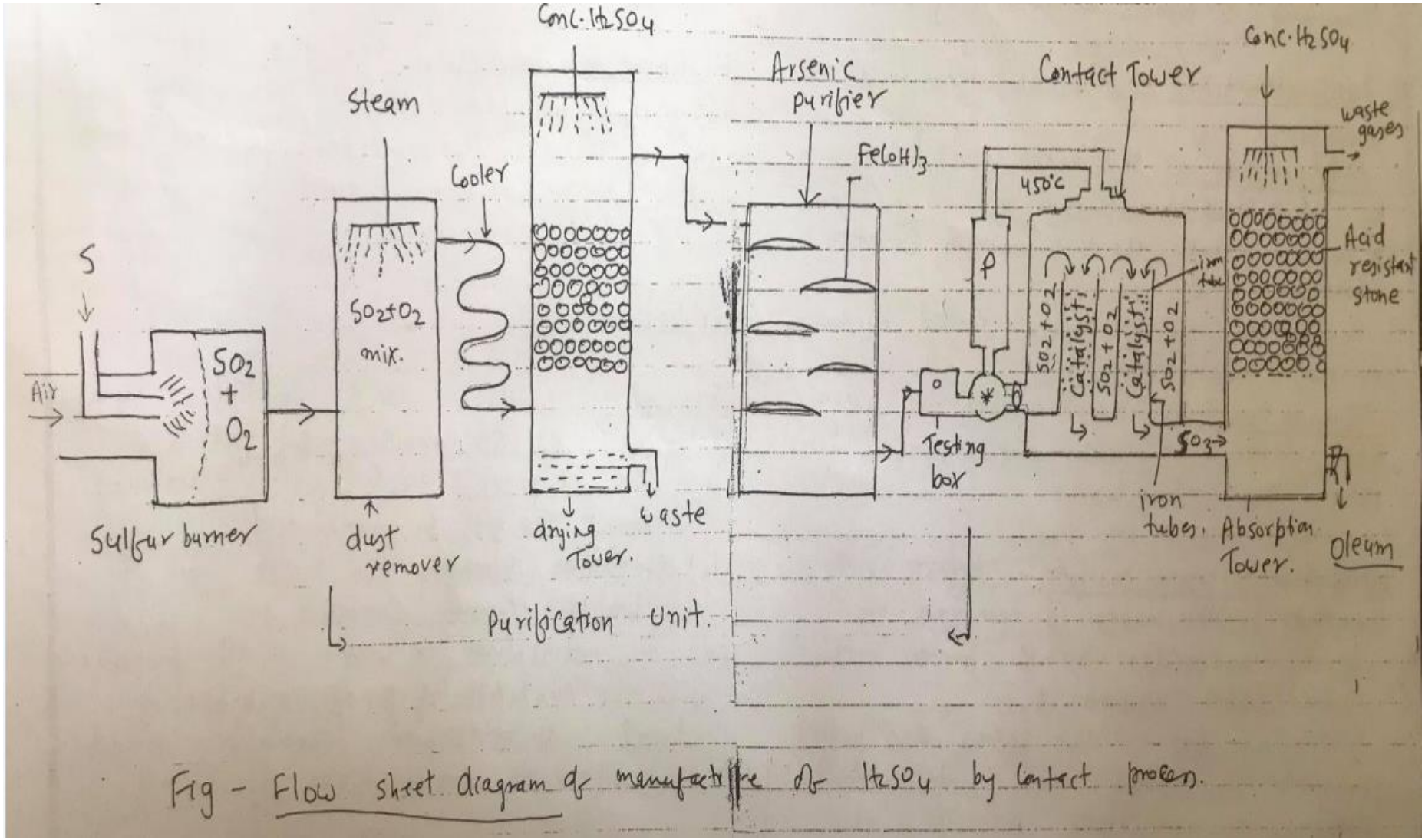

Fig - Flow sheet diagram of manufacture of H_2SO_4 by contact process.

The plant consists of

1) Sulfur burner - SO_2 is produced by roasting of pyrites or by burning sulphur.

2) Purification Unit - This unit consists of following parts.
i) Dust remover → It removes dust from gases by mechanical precipitation by allowing steam to come in makes the dust particles to settle down.
ii) Cooler → The gases are cooled by passing through cooling pipe.
iii) Drying Tower → Moisture from the gases are removed by passing conc. H_2SO_4 which is a dehydrating agent.

Manufacture of H_2SO_4 by Contact process contd….

iv) Arsenic Purifier - Arsenic oxide present in the gases is removed by ferric hydroxides which is present on the selves which absorb it.

v) Testing box - The gases are passed though the testing box to test that they are completely free from the impurities or not by using beam of light inside it.

3) Contact Tower- This is the most important tower where iron tubes are packed with catalyst V_2O_5. Here SO_2 is catalytically oxidized to SO_3.

4) Absorption Tower - From the contact tower, SO_3 is introduced to the absorption tower in which conc. H_2SO_4 is showered from the top forming oleum.

Properties

Physical Properties

i) H_2SO_4 is a colourless syrupy liquid of sp. gravity 1.84 at 15˚C.
ii) Its B.pt. is 338˚C and freezing pt. is -10˚C when it contains about 98.3% sulphuric acid.
iii) It fumes strongly in moist air & is highly corrosive.
iv) It dissolves in water in all proportions with the evolution of large quantities of heat. It is safer therefore to add the acid into water when diluting it.

Chemical Properties

i) Action of heat (Thermal decomposition)

On heating strongly it dissociates into SO_3 and H_2O

$H_2SO_4 \leftrightarrow H_2O + SO_3$

ii) Dehydrating action (Affinity for water)

Its affinity towards water is shown by the charring of organic matter like sugar, wood paper, oxalic acid, formic acid, alcohol and from copper sulphate it removes water of crystallization.

a) $C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + [H_2SO_4.11H_2O]$
Sugar

b) $(COOH)_2 + H_2SO_4 \rightarrow CO + CO_2 + [H_2SO_4.H_2O]$
Oxalic acid

c) $HCOOH + H_2SO_4 \rightarrow CO + [H_2SO_4.H_2O]$
Formic acid

d) $C_2H_5OH + H_2SO_4 \rightarrow C_2H_4 + [H_2SO_4.H_2O]$
(Alcohol) (Ethene)

e) $CuSO_4.5H_2O + H_2SO_4 \rightarrow CuSO_4 + [H_2SO_4.5H_2O]$
(Anhydrous copper sulphate)

iii) Oxidising action -

a) With metals like Zn, Fe, Mg, Al, tin etc, H_2SO_4 gives H_2 gas as follows.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow$

b) With metals like Pb, Ca, Hg, Ag H_2SO_4 gives SO_2 gas as follows.

$Cu + H_2SO_4 \rightarrow CuSO_{4\,+}\,2H$

$H_2SO_{4\,+}\,2H \rightarrow SO_2 + 2H_2O$

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

Similarly ,

$Pb + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_2$

Oxidising action of H_2SO_4 contd..

c) With non-metal → H_2SO_4 is an oxidising agent , it supplies nascent oxygen. H_2SO_4 oxidises number of non-metals like C, S, P etc.

With Carbon,

$H_2SO_4 \rightarrow H_2O + SO_2 + (O)] \times 2$

$C + 2(O) \rightarrow CO_2$

$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

With Sulphur,

$H_2SO_4 \rightarrow H_2O + SO_2 + (O)\ ] \times 2$

$S + 2(O\ ) \rightarrow SO_2$

$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$

Oxidising action of H_2SO_4 contd..

d) With Bromide & Iodides :- HI and HBr are oxidised to I_2 and Br_2 respectively with H_2SO_4

$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$

$2HI + [O] \rightarrow H_2O + I_2$

$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

Similarly ,

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

e) With Hydrogen sulphides - with H_2SO_4 , H_2S is oxidized to sulphur.

$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$

$H_2S + [O] \rightarrow H_2O + S$

$H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 + S$

iv) Action with salts of more volatile acids

with nitrites and nitrates, it gives different product.

$2NaNO_2 + H_2SO_4(dil) \rightarrow [Na_2SO_4 + 2HNO_2] \rightarrow Na_2SO_4 + NO + NO_2 + H_2O$

with carbonates, bicarbonates, sulphites, sulphides, thiosulphates, chlorides, floride, iodides, acetates, oxalates & phosphates, it gives following products.

$Na_2CO_3 + H_2SO_4(dil) \rightarrow [Na_2SO_4 + H_2CO_3] \rightarrow Na_2SO_4 + CO_2 + 2H_2O.$

$2NaHCO3 + H_2SO_4(dil) \rightarrow 2NaHSO_4 + 2H_2CO_3 \rightarrow [NaHSO_4 + 2CO_2 + 2H_2O]$

Action with salts of more volatile acids contd…

$Na_2SO_3 + H_2SO_4$ (dil.) → $[Na_2SO_4 + H_2SO_3]$ → $Na_2SO_4 + SO_2 + H_2O$

$Na_2S + H_2SO_4$ (dil.) → $Na_2SO_4 + H_2S$

$Na_2S_2O_3 + H_2SO_4$(dil.) → $[Na_2SO_4 + H_2SO_3 + S]$ → $Na_2SO_4 + SO_2 + H_2O + S$

$CaF_2 + H_2SO_4$ (Conc.) → $CaSO_4 + 2HF$

Calcium fluoride

$2NaCl + H_2SO_4$(Conc.) → $NaHSO_4 + HCl$

Action with salts of more volatile acids contd…

-With sod. iodide, bromide, sulphuric acid gives SO_2 also

$2NaI + 3H_2SO_4 \rightarrow 2NaHSO_4 + SO_2 + I_2 + 2H_2O$

$2NaBr + 3H_2SO_4 \rightarrow 2NaHSO_4 + SO_2 + Br_2 + 2H_2O$

-With pot. acetate, it gives pot. sulphate as follows.

$3CH_3COOK + \text{conc. } H_2SO_4 \rightarrow K_2SO_4 + 2CH_3COOH$

(Pot. Acetate) (Pot. Sulphate)

Chemical properties of H_2SO_4 contd..

v)Acidic properties

It is a dibasic acid and gives all the properties of hydrogen ion in solution. By neutralization with alkalies, it gives two series of salts (the normal) and acid sulphate salt.

$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

vi)Action with SO_3

SO_3 dissolves in conc. H_2SO_4 forming fuming oleum.

$H_2SO_4 + SO_3$ **dissolve**$\rightarrow H_2S_2O_7$ (fuming oleum)

Uses of sulphuric acid

Sulphuric acid is used in several industries. It is used

i) For the manufacture of chemical fertilizers, explosives, dyes, drugs and disinfectant.
ii) For the manufacture of paints.
iii) For the manufacture of synthetic fiber plastics and detergents.
iv) For petroleum refining.
v) For the lab as an important reagent & as a drying & dehydrating agent.