

10

Study of Compounds — Nitric Acid

SYLLABUS

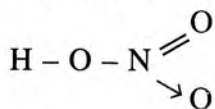
Nitric Acid : One laboratory method of preparation of nitric acid from potassium nitrate or sodium nitrate; Nitric acid as an oxidising agent.

Nitric Acid : Laboratory method of preparation of nitric acid from potassium nitrate or sodium nitrate; the laboratory method can be studied in terms of reactant, product, condition, equation, setting, diagram, precaution, collection, identification.

As an oxidising agent : its reaction with copper, carbon, sulphur.

Molecular formula : HNO_3

Relative molecular mass : 63



Structure of nitric acid

(Nitrogen shows valency of 5)

10.1 INTRODUCTION

The acid was formerly known as **aqua fortis** meaning *strong water*. It is so called because it reacts with nearly all metals. It can even dissolve silver which does not dissolve in other acids.

10.2 DISCOVERY

Glauber, in 1658, obtained nitric acid by distilling nitre, (potassium nitrate, KNO_3) with sulphuric acid.

Lavoisier, in 1776, proved that nitric acid contains oxygen.

Cavendish, in 1784, proved that it also contains hydrogen and nitrogen in addition to oxygen.

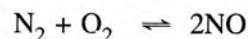
10.3 OCCURRENCE

In the **free** state, nitric acid is found in rain water, where it occurs in traces after lightning.

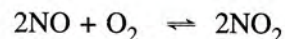
In the **combined state**, it is found in the form of metallic nitrates such as Chile saltpetre (NaNO_3), nitre (KNO_3), or calcium nitrate [$\text{Ca}(\text{NO}_3)_2$].

Formation of nitric acid in atmosphere

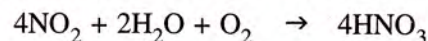
1. During *lightning discharge*, the nitrogen present in the atmosphere reacts with the oxygen to form nitric oxide.



2. Nitric oxide is further *oxidised* to nitrogen dioxide.



3. This nitrogen dioxide *dissolves in atmospheric moisture* or *rain water* in the presence of oxygen of the air and forms nitric acid in the **free state**, which is washed down by the rain and combines with the salt present on the surface of the earth.



*The conversion of free atmospheric nitrogen into useful nitrogenous compounds in the soil is known as **fixation of atmospheric nitrogen**.*

10.4 LABORATORY PREPARATION OF NITRIC ACID

Reactants : It is obtained by distilling conc. sulphuric acid with nitrates of potassium KNO_3 (nitre) or sodium NaNO_3 (Chile saltpetre).

Procedure : A mixture of equal parts, by weight, of potassium/sodium nitrate and concentrated sulphuric acid is heated gently to 180°C - 200°C in a glass retort (Fig 10.1). Sulphuric acid is a non-volatile acid and produces volatile nitric acid on reacting with potassium nitrate or sodium nitrate.

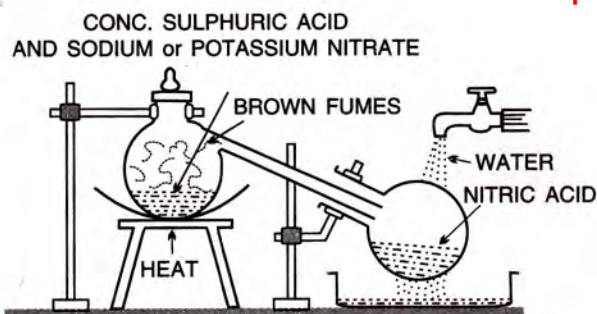


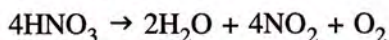
Fig. 10.1 Laboratory preparation of nitric acid

Reactions :

Nitre/Chile saltpetre	+ Sulphuric acid	→	Potassium/ Sodium bisulphate	+ Nitric acid
KNO_3	+ H_2SO_4 conc.	$\xrightarrow{<200^\circ\text{C}}$	KHSO_4	+ HNO_3
NaNO_3	+ H_2SO_4 conc.	$\xrightarrow{<200^\circ\text{C}}$	NaHSO_4	+ HNO_3

Collection : The vapours of nitric acid are condensed to a **light yellow liquid** by chilling the receiver with running cold water.

Note : Pure acid is colourless but the acid obtained in the laboratory is slightly yellow. The yellow colour is due to dissolution of reddish brown coloured **nitrogen dioxide gas** in the acid. This gas is produced due to the thermal decomposition of a portion of nitric acid.

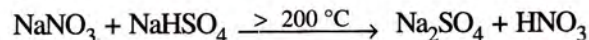
**The yellow colour of the acid is removed :**

- If *dry air* or CO_2 is bubbled through the yellow acid, the latter turns colourless because it drives out NO_2 from warm acid which is further oxidised to nitric acid.
- By addition of excess of water, nitrogen dioxide gas dissolves in water and thus the yellow colour of the acid is removed. The reaction is the reverse of the decomposition of nitric acid.

Precautions :

- All glass apparatus is used because nitric acid vapours *attack rubber and cork*.
- Conc. HCl is not used in place of conc. H_2SO_4 because HCl is *volatile and hence nitric acid vapours will carry HCl vapours*.
- The temperature of the reaction should not

exceed 200°C , because sodium sulphate formed at higher temperature forms a hard crust which sticks to the walls of the retort and is difficult to remove, although the yield of HNO_3 is higher.



The higher temperature

- may damage the glass apparatus,
- decomposition of nitric acid can also occur,
- Wastage of fuel.

10.5 PROPERTIES OF NITRIC ACID**(A) Physical properties**

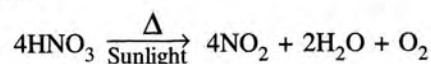
- Colour :** It is a colourless liquid (98% concentration) but the commercial nitric acid (68% concentration) is yellowish *brown in colour*.
- Odour :** Suffocating smell.
- Taste :** Acidic (sour taste).
- Nature :** *Hygroscopic and fumes in air*. Hence, the bottle containing nitric acid should always be stoppered.
- Density :** 1.54 g/cm^3 (98%) but the commercial nitric acid (68%) has lower density 1.42 g/cm^3 .
- Boiling point and melting point :** It boils at 86°C and melts at -42°C .

An aqueous solution of nitric acid (68% concentration) forms a **constant boiling mixture** at 121°C .

- Solubility :** Soluble in water in all proportions.
- Physiological action :** Non-poisonous. It has a corrosive action on the skin and causes painful blisters. It stains the skin yellow as it reacts with protein of the skin and forms **xanthoproteic acid**.

(B) Chemical properties

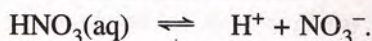
- Stability :** Pure nitric acid is unstable to heat or sunlight. It decomposes to give yellow solution due to the formation of nitrogen dioxide. Thus, 100% nitric acid is not generally used.



In the presence of sunlight, nitric acid decomposes even at room temperature. *The nitric acid stored in a bottle turns yellow. This colour is due to dissolved NO₂ in HNO₃. To avoid the decomposition, nitric acid is normally stored in coloured bottles.*

(2) Acidic properties : Nitric acid is a very strong **monobasic acid**.

HNO₃ ionises almost completely in aqueous solution to produce hydrogen ions and nitrate ions.



(i) **It turns :**

- blue litmus red,
- methyl orange pink,
- phenolphthalein remains colourless.

(ii) **Reaction with alkalis :**

It neutralises alkalis to form salt and water.

All metallic oxides and hydroxides react with dilute nitric acid to form their respective soluble metallic nitrates and water only.

Base	+	Acid (dil)	→	Salt	+	Water
K ₂ O	+	2HNO ₃	→	2KNO ₃	+	H ₂ O
CuO	+	2HNO ₃	→	Cu(NO ₃) ₂	+	H ₂ O
ZnO	+	2HNO ₃	→	Zn(NO ₃) ₂	+	H ₂ O
NaOH	+	HNO ₃	→	NaNO ₃	+	H ₂ O
Fe(OH) ₃	+	3HNO ₃	→	Fe(NO ₃) ₃	+	3H ₂ O
Mg(OH) ₂	+	2HNO ₃	→	Mg(NO ₃) ₂	+	2H ₂ O

(iii) **Reaction with carbonates and bicarbonates :**

It reacts with carbonates and bicarbonates to give salt, water and carbon dioxide.

Carbonate/ Bicarbonate	+	Acid	→	Salt	+	Water	+	Carbon dioxide
CaCO ₃	+	2HNO ₃	→	Ca(NO ₃) ₂	+	H ₂ O	+	CO ₂ ↑
NaHCO ₃	+	HNO ₃	→	NaNO ₃	+	H ₂ O	+	CO ₂ ↑
Na ₂ CO ₃	+	2HNO ₃	→	2NaNO ₃	+	H ₂ O	+	CO ₂ ↑
CuCO ₃	+	2HNO ₃	→	Cu(NO ₃) ₂	+	H ₂ O	+	CO ₂ ↑

(iv) **Action with metallic sulphites and bisulphites :**

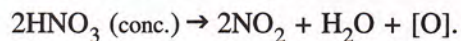
Metallic sulphites and bisulphites react with dilute nitric acid to form their soluble metallic nitrates, water and sulphur dioxide gas.

Metallic sulphite	+	Nitric acid (dil)	→	Metallic nitrate	+	Water	+	SO ₂ (g)
K ₂ SO ₃	+	2HNO ₃	→	2KNO ₃	+	H ₂ O	+	SO ₂ (g)
CuSO ₃	+	2HNO ₃	→	Cu(NO ₃) ₂	+	H ₂ O	+	SO ₂ (g)
Ca(HSO ₃) ₂	+	2HNO ₃	→	Ca(NO ₃) ₂	+	2H ₂ O	+	2SO ₂ (g)

(3) Oxidising properties : Nitric acid vigorously oxidises non-metals, metals, inorganic compounds and organic substances.

Nitric acid itself undergoes reduction to form different reduction products like NO, NO₂, N₂O, etc., These products depend on the acid concentration and the temperature of the reaction.

Oxidising properties are due to nascent oxygen which it gives on decomposition.



Nitric acid is a powerful oxidising agent and the nascent oxygen formed on decomposition oxidises hydrogen to water.

(i) **Action on non-metals**

Non-metal	Acid [conc.]	→	Oxidised product	Water	Nitrogen dioxide
a. Carbon					
C	+	4HNO ₃	→	CO ₂	+ 2H ₂ O + 4NO ₂
b. Sulphur					
S	+	6HNO ₃	→	H ₂ SO ₄	+ 2H ₂ O + 6NO ₂
c. Phosphorus					
P ₄	+	20HNO ₃	→	4H ₃ PO ₄	+ 4H ₂ O + 20NO ₂

(ii) **Action on metals**

Nitric acid reacts with all metals except gold and platinum. The action of nitric acid on metals depends on the temperature and concentration of nitric acid.

(a) Cold and dilute nitric acid oxidises metals to their nitrates and liberates nitric oxide.

Metal	Oxidised product
1. Copper	
3Cu	+ 8HNO ₃ → 3Cu(NO ₃) ₂ + 4H ₂ O + 2NO
2. Zinc	
3Zn	+ 8HNO ₃ → 3Zn(NO ₃) ₂ + 4H ₂ O + 2NO
3. Iron	
3Fe	+ 8HNO ₃ → 3Fe(NO ₃) ₂ + 4H ₂ O + 2NO

(b) Concentrated nitric acid [or hot dilute nitric acid] – liberates nitrogen dioxide.

Metal	Oxidised product
1. Copper $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$	
2. Zinc $\text{Zn} + 4\text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$	
3. Iron $\text{Fe} + 6\text{HNO}_3 \rightarrow \text{Fe}(\text{NO}_3)_3 + 3\text{H}_2\text{O} + 3\text{NO}_2$	

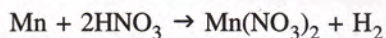
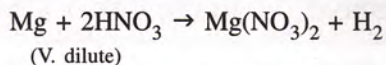
(c) Metals like iron, aluminium, cobalt and nickel become passive (inert) when treated with pure concentrated nitric acid.

It is due to the formation of extremely thin layer of insoluble metallic oxide (passivity) which stops the reaction.

Passivity can be removed, by rubbing the surface layer with sand paper, or by treating with strong reducing agents.

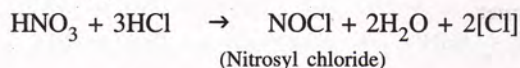
Note : Dilute Nitric acid is generally considered a typical acid except for its reaction with metals since it does not liberate hydrogen. It is a powerful oxidising agent and the nascent oxygen formed oxidises the hydrogen to water.

(d) Very dilute (about 1%) **acid** reacts with magnesium and manganese at room temperature to give their nitrates and hydrogen gas. Since the oxidising action of the acid is much reduced due to dilution.



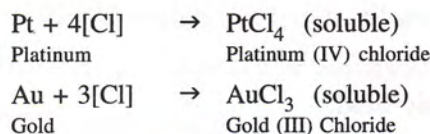
These reactions prove that nitric acid contains hydrogen.

(4) Reaction as aqua regia : Conc. nitric acid (1 part by volume) when mixed with conc. hydrochloric acid (3 parts by volume) gives a mixture called **aqua regia** (meaning **royal water**).



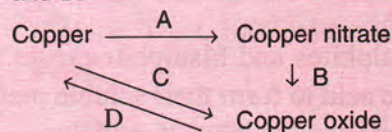
Nitric acid oxidises hydrochloric acid to chlorine.

This mixture (*aqua regia*) reacts even with noble metals like gold and platinum to give their chlorides. Aqua regia contains nascent chlorine which attack these metals.



Intext Questions

- What is : (a) aqua fortis, (b) aqua regia (c) Fixation of Nitrogen ?
- During thunderstorm, rain water contains nitric acid. Explain with reactions.
- (a) Write a balanced chemical equation for the laboratory preparation of nitric acid.
(b) In the preparation of nitric acid from KNO_3 , concentrated hydrochloric acid is not used in place of concentrated sulphuric acid. Explain why ?
(c) Conc. nitric acid prepared in laboratory is yellow in colour. Why ? How is this colour removed ?
(d) Give reasons for the following :
In the laboratory preparation of nitric acid, the mixture of concentrated sulphuric acid and sodium nitrate should not be heated very strongly above 200°C .
- Nitric acid cannot be concentrated beyond 68% by the distillation of a dilute solution of HNO_3 . State the reason.
- What is passive iron ? How is passivity removed?
- Name the products formed when :
(a) carbon and conc. nitric acid is heated,
(b) dilute HNO_3 is added to copper.
- Give two chemical equations for each of the following :
(a) Reactions of nitric acid with non-metals.
(b) Nitric acid showing as acidic character.
(c) Nitric acid acting as oxidising agent.
- Write balanced equations and name the products formed when :
(a) sodium hydrogen carbonate is added to nitric acid,
(b) cupric oxide reacts with nitric acid,
(c) zinc reacts with dilute nitric acid,
(d) concentrated nitric acid is heated.
- Write equation for the following conversions A, B, C and D.



10. How will you prepare the following from nitric acid ?

- (a) Sodium nitrate (b) Copper nitrate
(c) Lead nitrate (d) Magnesium nitrate
(e) Ferric nitrate (f) Aqua regia

11. Correct the following, if required : ✓

- (a) HNO_3 is a strong reducing agent.
(b) NaNO_3 gives NO_2 and O_2 on heating.
(c) Constant boiling nitric acid contains 80% nitric acid by weight.
(d) Nitric acid remains colourless even when exposed to light.

10.6 USES OF NITRIC ACID

(i) To etch designs on copper and brassware.

Reason : Nitric acid acts as a *solvent* for a large number of metals except noble metals.

(ii) To purify gold.

Reason : Gold may contain Cu, Ag, Zn, Pb, etc., as *impurities* which dissolve in nitric acid.

(iii) It acts as a rocket fuel oxidant.

(iv) In preparation of fertilizers.

Calcium nitrate $\text{Ca}(\text{NO}_3)_2$,

Ammonium nitrate NH_4NO_3 ,

Nitro chalk $[\text{NH}_4\text{NO}_3 + \text{CaCO}_3]$ and

Basic calcium nitrate $\text{CaO} \cdot \text{Ca}(\text{NO}_3)_2$.

(v) In the preparation of aqua regia which dissolves noble metals.

Industrial uses : In the manufacture of :

I. Explosives like T.N.T.

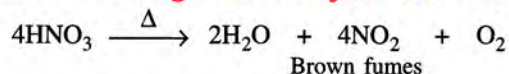
II. Synthetic fibres like artificial silk, nylon, celluloid, plastics, photographic film, etc.

III. Important compounds like nitrates of potassium, ammonium, silver, etc.

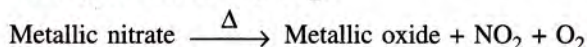
IV. Dyes/Drugs/Perfumes.

10.7 TESTS FOR NITRIC ACID AND NITRATES

1. **Conc. nitric acid gives brown fumes on heating.**

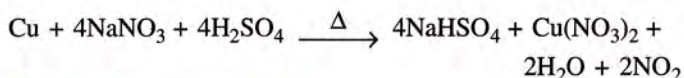
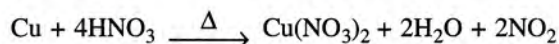


2. **Nitrates** (other than potassium, sodium and ammonium) produce **reddish brown fumes of nitrogen dioxide** $[\text{NO}_2]$.



3. **On adding copper to HNO_3 or acidified nitrates**

Dense reddish brown fumes of nitrogen dioxide $[\text{NO}_2]$ are evolved.



4. **Brown Ring Test**

Procedure : To the aq. solution of a nitrate or nitric acid:

- (i) Add freshly prepared saturated solution of iron [II] sulphate.
- (ii) Now add conc. sulphuric acid carefully from the sides of the test tube, so that it should not fall dropwise in the test tube.
- (iii) Cool the test tube in water.
- (iv) A brown ring appears at the junction of the two liquids.

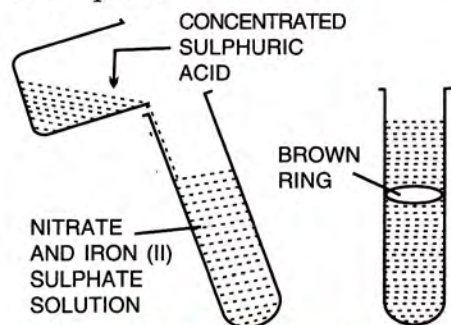
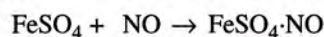
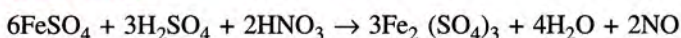


Fig. 10.2 Brown ring test

Reaction :

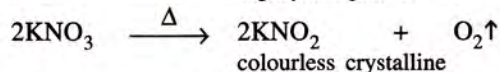
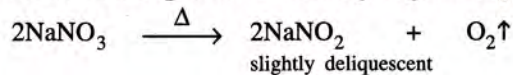


[Nitroso ferrous sulphate, a brown compound]

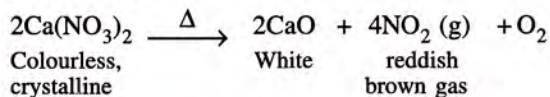
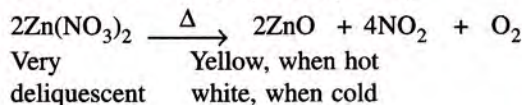
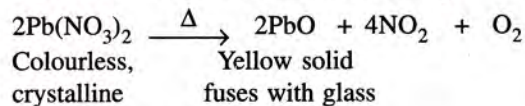
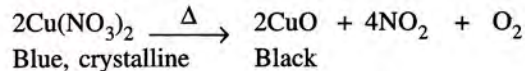
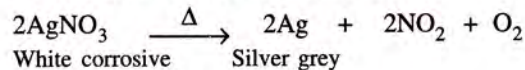
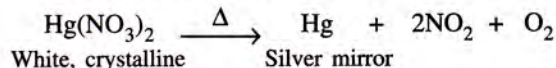
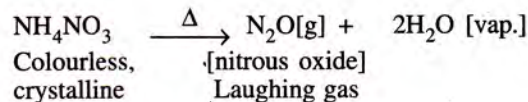
- Note :**
- (i) A freshly prepared ferrous sulphate solution is used, because on exposure to the atmosphere, it is oxidised to ferric sulphate which will not give the brown ring.
 - (ii) The brown ring of nitroso ferrous sulphate is formed at the junction of the two liquids. The conc. sulphuric acid being heavier settles down and the ferrous sulphate layer remains above it resulting in the formation of brown ring at the junction.
 - (iii) The brown ring of nitroso ferrous sulphate decomposes on disturbing the test tube. The heat evolved decomposes the unstable brown ring.

10.8 EFFECTS OF HEAT ON NITRATES**(i) Sodium and potassium nitrates or alkali metal nitrates.**

When heated, they melt into colourless liquids which decomposes on heating to give oxygen gas.



When a glowing splinter is brought near the molten liquid, it bursts into flames because oxygen is formed.

(ii) All other nitrates except those of silver and mercury decompose into their oxides, nitrogen dioxide and oxygen.**1. Calcium nitrate****2. Zinc nitrate (slightly decrepitates)****3. Lead nitrate (decrepitates on heating)****4. Copper nitrate****(iii) Silver and mercury nitrates :** They are white corrosive salts, which decompose into their respective metals, nitrogen dioxide and oxygen.**1. Silver nitrate (Lunar caustic)****2. Mercuric nitrate****(iv) Ammonium nitrate :** Ammonium nitrate decomposes explosively leaving behind no residue.**EXERCISE****1. Choose the correct answer :**

(a) The nitrate salt which does not give a mixture of NO_2 and O_2 on heating is :

- (i) AgNO_3 , (ii) KNO_3 ,
(iii) $\text{Cu}(\text{NO}_3)_2$, (iv) $\text{Zn}(\text{NO}_3)_2$.

(b) The chemical used in the brown ring test is :

- (i) CuSO_4 , (ii) FeSO_4 ,
(iii) $\text{Fe}_2(\text{SO}_4)_3$, (iv) ZnSO_4 .

(c) Lead nitrate decomposes on heating to give :

- (i) NO , (ii) N_2O ,
(iii) NO_2 , (iv) N_2O_5 .

2. Name :

- (a) a nitrate of metal which on heating does not give nitrogen dioxide.
(b) a nitrate which on heating leaves no residue behind.
(c) a metal nitrate which on heating is changed into metal oxide.
(d) a metal nitrate which on heating is changed into metal.
(e) a solution which absorbs nitric oxide.
(f) the oxide of nitrogen which turns brown on exposure to air. How is it prepared ?

3. Mention three important uses of nitric acid. Give the property of nitric acid involved in the use.

4. (a) Explain with the help of a balanced equation, the brown ring test for nitric acid.

(b) Why is freshly prepared ferrous sulphate solution used for testing the nitrate radical in the brown ring test ?

5. From the following list of substances, choose one substance in each case which matches the description given below :

Ammonium nitrate, calcium hydrogen carbonate, copper carbonate, lead nitrate, potassium nitrate, sodium carbonate, sodium hydrogen carbonate, zinc carbonate.

- (a) A nitrate which gives off only oxygen when heated.
(b) A nitrate which on heating decomposes into dinitrogen oxide [nitrous oxide] and steam.
(c) A nitrate which gives off oxygen and nitrogen dioxide when heated.

6. The action of heat on the blue crystalline solid X, gives a reddish brown gas Y, a gas which re-lights a glowing splint and leaves a black residue. When gas Z, which has

a rotten egg smell, is passed through a solution of X, a black ppt. is formed.

- Identify X, Y and Z.
- Write equation for action of heat on X.
- Write equation between solution of X and gas Z.

7. X, Y and Z are three crystalline solids which are soluble in water and have a common anion.

To help you to identify X, Y and Z, you are provided with the following experimental observations. Copy and complete the corresponding inferences in (a) to (e).

- A reddish-brown gas is obtained when X, Y and Z are separately warmed with concentrated sulphuric acid and copper turning added to the mixture.

INFERENCE 1 : The common anion is the ion.

- When X is heated, it melts and gives off only one gas which re-lights a glowing splint.

INFERENCE 2 : The cation in X is either or

- The action of heat on Y produces a reddish-brown gas and a yellow residue which fuses with the glass of the test tube.

INFERENCE 3 : The metal ion present in Y is the ion.

- When Z is heated, it leaves no residue. Warming Z with sodium hydroxide solution liberates a gas which turns moist red litmus paper blue.

INFERENCE 4 : Z contains the cation.

- Write the equations for the following reactions:

(1) X and concentrated sulphuric acid (below 200° C). (One equation only for either of the cations given in INFERENCE 2).

(2) Action of heat on Y.

(3) Concentrated nitric acid is added to copper turnings kept in a beaker.

8. (a) Dilute nitric acid is generally considered a typical acid except for its reaction with metals. In what way is dilute nitric acid different from other acids when it reacts with metals?

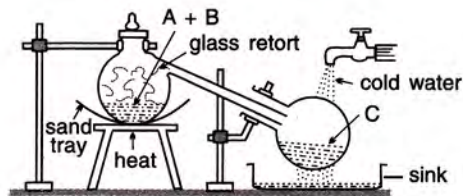
- Write the equation for the reaction of dilute nitric acid and conc. nitric acid with copper.

9. Explain why

(a) *Only all-glass apparatus should be used for the preparation of nitric acid by heating concentrated sulphuric acid and potassium nitrate.*

(b) Nitric acid is kept in a reagent bottle for a long time.

10. The figure given below illustrates the apparatus used in the laboratory preparation of nitric acid.



- Name A (a liquid), B (a solid) and C (a liquid). (Do not give the formulae).

(b) Write an equation to show how nitric acid undergoes decomposition.

(c) Write the equation for the reaction in which copper is oxidized by concentrated nitric acid.

11. (a) A dilute acid B does not normally give hydrogen when reacted with metals but does give a gas when reacts with copper. Identify B. Write equation with copper.

(b) Complete the table :

Name of Process	Inputs	Equation	Output
	Ammonia + Air		Nitric acid

(c) What is the property of nitric acid which allows it to react with copper.

2012

(a) Name – the gas produced when copper reacts with conc. HNO_3 .

(b) State observation – zinc nitrate crystals are strongly heated.

(c) Correct the statement :

Magnesium reacts with nitric acid to liberate hydrogen gas.

(d) Iron is rendered passive with fuming HNO_3 . Give reason.

(e) Give balanced equation for dilute nitric acid and copper carbonate.

2013

(a) Identify the gas evolved when.

(i) Sulphur is treated with conc. nitric acid.

(ii) A few crystals of KNO_3 are heated in a hard glass test tube.

(b) State two relevant observations for lead nitrate crystals are heated in a hard glass test tube.

(c) Give a balanced equation for : oxidation of carbon with conc. HNO_3 .

2014

(a) Fill in the blank :

Cold dil. nitric acid reacts with copper to form (hydrogen, nitrogen dioxide, nitric oxide).

(b) Give balanced equations for the following

(i) Laboratory preparation of nitric acid.

(ii) Action of heat on a mixture of copper and nitric acid.