Acid Rains

Acid rains is rainfall whose pH is less than 5.6 , the value(5.6) typically observed, due to the presence of dissolved carbon dioxide. Acid rain is caused by nitrogen oxide and sulfur dioxide produced by both natural processes and the combustion of fossil fuels. Eventually, these oxides react with oxygen and water to give nitric acid and sulfuric acid.

How is it caused?

Acid rain is caused by emissions of sulfur dioxide and nitrogen oxide , which react with the water molecules in the atmosphere to produce acids. Nitrogen oxide can also be produced naturally by lightning strikes and sulfur dioxide is produce by volcanic eruptions. The chemicals in acid rain can cause paint to peel, corrosion of steel structures , and erosion of stone statues.

Gas	**Natural Sources**	**Concentration**
Carbon dioxide CO_2	Decomposition	355 ppm
Nitric oxide NO	Electric discharge	0.01 ppm
Sulfur dioxide SO_2	Volcanic gases	0-0.01 ppm

Table 1 :Carbon dioxide, produced in the decomposition of organic material, is the primary source of acidity in unpolluted rainwater.

Humans cause many combustion processes that dramatically increase the concentrations of acid-producing oxides in the atmosphere. Although CO_2 is present in a much higher concentration than NO and SO_2, CO_2 does not form acid to the same extent as the other two gases. Thus, a large increase in the concentration of NO and SO_2 significantly affects the pH of rainwater, even though both gases are present at much lower concentration than CO_2.

Gas	**Non-Natural Sources**	**Concentration**
Nitric oxide NO	Internal Combustion	0.2 ppm
Sulfur dioxide SO_2	Fossil-fuel Combustion	0.1 - 2.0 ppm

Table 2 : Nitric oxide NO and Sulfur dioxide SO_2 is the primary source of acidity in polluted rainwater.

The Chemistry of Acid Rain

The term **acid rain** is actually somewhat misleading because even pure rainwater collected in areas remote from civilization is slightly acidic (pH ≈ 5.6) due to dissolved carbon dioxide, which reacts with water to give carbonic acid, a weak acid:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Typical pH values for rain in the continental United States now range from 4 to 4.5, with values as low as 2.0 reported for areas such as Los Angeles.

Carbon dioxide reacts with water to form carbonic acid

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad \text{…….. (1)}$$

Carbonic acid then dissociates to give the hydrogen ion (H^+) and the hydrogen carbonate ion (HCO_3^-).

$$H_2CO_3 \longrightarrow H^+ + HCO_3^- \qquad \text{…….(2)}$$

The ability of H_2CO_3 to deliver H^+ is what classifies this molecule as an acid, thus lowering the pH of a solution.

What is the source of the increased acidity in rain and snow?

Chemical analysis shows the presence of large quantities of sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions, and a wide variety of evidence indicates that a significant fraction of these species come from nitrogen and sulfur oxides produced during the combustion of fossil fuels.

Nitric oxide (NO):

At the high temperatures found in both internal combustion engines and lightning discharges, molecular nitrogen and molecular oxygen react to give nitric oxide:

$$N_{2(g)} + O_{2(g)} \xrightarrow{\text{lightning}} 2NO_{(g)}$$

Nitric oxide then reacts rapidly with excess oxygen to give nitrogen dioxide, the compound responsible for the brown color of smog:

$$NO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$$

When nitrogen dioxide dissolves in water, it forms a 1:1 mixture of nitrous acid and nitric acid:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

Because molecular oxygen eventually oxidizes nitrous acid to nitric acid, the overall reaction is :

$$2HNO_2\ (aq) + O_2 \rightarrow 2HNO_3(aq)$$

$$HNO_3(aq) \rightleftharpoons NO_3^- + H^+$$

Sulfur dioxide SO_2 :

Most acidity is accounted for by the presence of sulfuric acid (H_2SO_4) in rainwater . Large amounts of sulfur dioxide have always been released into the atmosphere by natural sources, such as volcanoes, forest fires, and the microbial decay of organic materials . Unfortunately, the burning of fossil fuels seems to have tipped the balance. Many coals contain as much as 5%–6% pyrite (FeS_2) by mass, and fuel oils typically contain at least 0.5% sulfur by mass. Since the mid-19th century, these fuels have been burned on a huge scale to supply the energy needs of modern industrial society, releasing tens of millions of tons of additional SO_2 into the atmosphere annually. In addition, roasting sulfide ores to obtain metals such as zinc and copper produces large amounts of SO_2 via reactions such as :

$$ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

Regardless of the source, the SO_2 dissolves in rainwater to give sulfurous acid , which is eventually oxidized by oxygen to sulfuric acid .

$$SO_{2(g)} \xrightarrow{O_2} SO_{3(g)} \xrightarrow{H_2O} H_2SO_4$$

Sulfuric acid is a strong acid, so it readily dissociates in water, to give an H^+ ion and an HSO_4^- ion

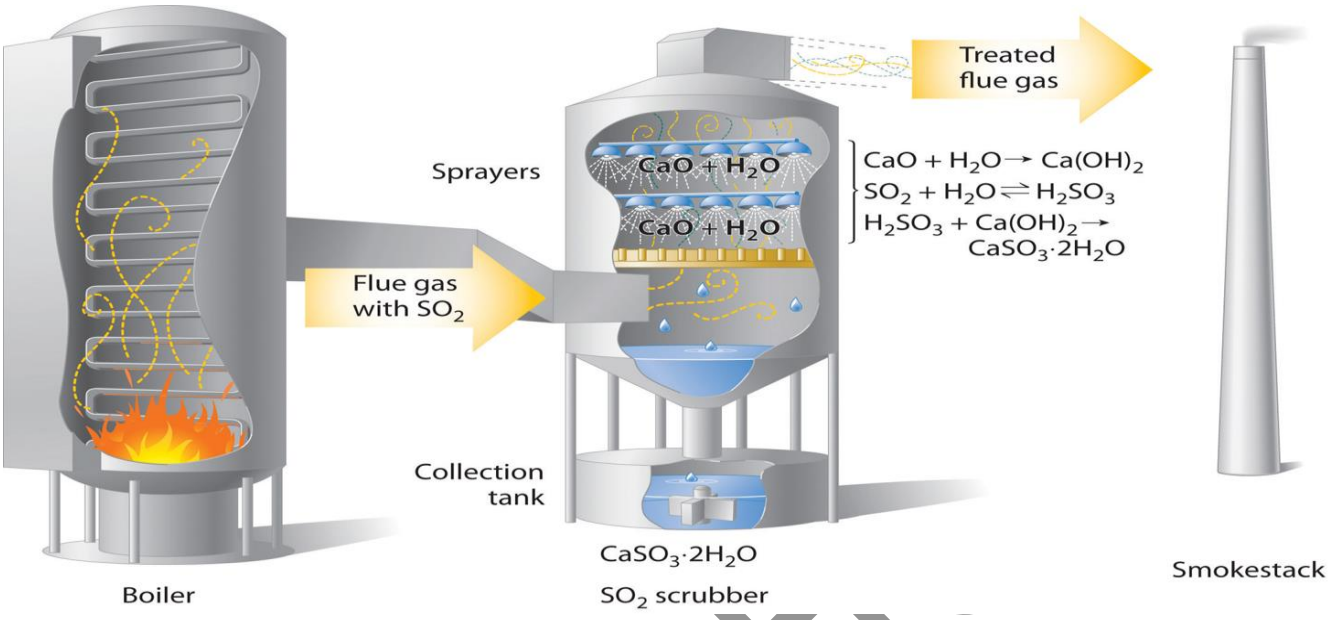
$$H_2SO_4 \longrightarrow HSO_4^- + H^+$$

The HSO_4^- ion may further dissociate to give H^+ and SO_4^{2-}

$$HSO_4^- \longrightarrow SO_4^{2-} + H^+$$

Thus, the presence of H_2SO_4 causes the concentration of H^+ ions to increase dramatically, and so the pH of the rainwater drops to harmful levels.

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO. For example, coal-burning power plants now use SO_2 "scrubbers," which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$)



Fig(1): Schematic Diagram of a Wet Scrubber System .

How acid rain affects the environment ?

Acid rain is an extremely destructive form of pollution , and the environment suffers from its effects . Trees , , forests ,lakes , animals , and plants suffer from acid rain .

Trees: The needles and leaves of the trees turn brown and fall off . Trees can also suffer from stunted growth ; and have damaged bark and leaves , which makes them vulnerable to weather , disease , and insects .

Forests : Most of the effects on forests are subtle. Acid deposition may influence forest vegetation and soils. Acid rain weakens the trees' natural defenses, making them more vulnerable to diseases. Acid rain may remove soil nutrients such as calcium and magnesium from soils in high elevation forests. Acid rain may also cause **Forest die** (**deforestation).**

Algae: Acid rain deposits nitrates that can lead to increases in nitrogen in ecosystems. Nitrogen is an important plant nutrient, Nitrates can remove additional calcium and magnesium from the soils. Continued nitrogen deposition may alter other aspects of the nutrient balance in ecosystems and alter the chemistry of nearby lakes and streams . Excess nitrogen may cause eutrophication (over nourishment) in areas where rivers enter the ocean. This may lead to unwanted growth of algae and other nuisance plants.

Fishes:

Many species of fish are not able to survive in acidic water. Acid rain affects lakes and streams in two ways: chronic and episodic. Chronic, or long-term acidification results from years of acidic rainfall. It reduces the alkalinity (buffering capacity) and increases the acidity of the water. Chronic acidification may reduce the levels of nutrients such as calcium, which, over time, may weaken the fish and other plants and animals in an aquatic ecosystem. Episodic acidification is a sudden jump in the acidity of the water. This can result from a heavy rainstorm.This may lead to high concentrations of substances such as aluminum, which may be toxic to fish.

Questions on Acidity of Rainwater

- **Write a balanced chemical equation for the dissociation of nitric acid in water.**
  - $HNO_3(aq) \longrightarrow NO_3^- + H^+$
- **What causes such a dramatic increase in the acidity of rain relative to pure water?**
  - The answer lies within the concentrations of nitric oxide and sulfur dioxide in polluted air. The concentrations of these oxides are much higher than in clean air.
- **Acid rain is caused by increase in the atmospheric concentration of:**
  - NO and SO_2
- **What is the main source or sources of acid rain?**

A) Antartica B) Sewers C) Magneseum oxide D) Nitrogen oxide and Sulfer dioxide

- **The following effects are caused by acid rain:**

A) destruction of the ozone layer . B) heart diseases . C) corrosion of buildings .

D) deforestation.