Gases and Atmospheric Chemistry

SCH3U_2016

The earth's atmosphere is about 900 km thick but living things are confined to a thin layer extending to only 3.2 km above the surface. It is in this layer that most pollutants gather.

One of the principal problems facing our society today stems from chemical reactions which occur in our environment which do not simply disappear. These environmental problems are due to human cause.
The main source of air pollution is the burning of fossil fuels in houses, factories electric generating stations, and refineries, and vehicle engines.

When burned they produce soot, smoke, a mixture of gases including sulphur dioxide, SO_2, oxides of nitrogen, NO_x, carbon monoxide, CO, and various other hydrocarbons, C_xHy.

These pollutants rise on warm air currents.

Some remain airborne for a long time and are carried hundreds of kilometers by the wind, some enter clouds and fall back to earth as rain (known as **wet deposition or acid rain**), and some fall back to earth as **dry deposition**.

Acid Deposition: Acid Rain

Acid deposition is formed when nitrogen or sulphur oxides dissolve in water to form $HNO_{3(l)}$, $HNO_{2(l)}$, $H_2SO_{4(l)}$, and $H_2SO_{3(l)}$.

Normal rain is acidic because of dissolved $CO_{2\,(g)}$, which dissolves in water to form the weak acid carbonic acid, $H_2CO_{3(aq)}$ and has a pH = 5.6.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

carbonic acid, $H_2CO_{3(aq)}$, ionizes according to the following :

$$H_2CO_{3(aq)} \rightleftharpoons H^{+1}_{(aq)} + HCO_3^{-1}{}_{(aq)}$$

This gives a solution with a pH = 5.6.

Acid rain has a pH below 5.6, usually, (pH = 2 – 5), and therefore contains additional acids.

The main causes of acid rain are the oxides of sulphur and nitrogen, these being the *primary pollutants.*

When the oxides of sulphur and nitrogen dissolve in water to produce the *secondary pollutant*: the acid rain.

Acid deposition: is term used to describe acid rain and also includes all the acidic components as the gases and the precipitates that leave the atmosphere.
It is a form of acid deposition in which acids are dissolved in rain, fog, dew, or snow.

Examples of wet acid deposition: rain, snow, hail, sleet, fog, mist, dew

Examples of dry acid deposition: acidifying gases, particles, dust, smoke

Sulphur oxides

sulphur dioxide is emitted by:
Impurities of sulphur occur in crude oil, coal, natural gas, and gasoline. Burning of fuels (cars, coal, power stations to drive turbines, incineration, forest fires, volcanoes): e.g. Noranda, Algoma Steel, INCO) results in the formation of oxides of sulphur.

Sulphur combines with oxygen gas in the atmosphere to produce sulphur dioxide:

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

Sulphur dioxide, a colourless gas with a pungent odour, dissolves in water to form sulphurous acid:

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$

Sulphur dioxide can also combine with more oxygen gas in the atmosphere to produce sulphur trioxide:

$$2SO_{2\,(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

Sulphur trioxide combines with water in the atmosphere to produce diluted sulphuric acid which falls as acid rain:

$$2SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

Internal combustion engines operate at temperatures high enough to produce oxides of nitrogen from nitrogen and oxygen gas.

Same reactions occur with nitrogen oxides which combine with water vapour in the atmosphere to produce nitrous acid, $HNO_{2(aq)}$ and nitric acid, $HNO_{3(aq)}$.

Nitrogen monoxide, NO, is produced mainly from internal combustion engines, where the burning of fuels release heat energy thus allowing the nitrogen gas and oxygen gas to combine:

$$N_{2\,(g)} + O_{2(g)} \longrightarrow NO_{(g)} \qquad \Delta H = +\,181\ kJ\ mol^{-1}$$

Similarly, the toxic nitrogen dioxide, $NO_{2\,(g)}$ gas is formed:

$$N_{2\,(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)}$$

Nitrogen dioxide can also be formed when nitrogen monoxide undergoes oxidation:

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

Nitrogen dioxide dissolves in water to form a mixture of nitrous acid and nitric acid:

$$2NO_{2(g)} + H_2O_{(l)} \longrightarrow HNO_{2(aq)} + HNO_{3(aq)}$$

Both nitric acid and sulphuric acid are strong acids and so ionize completely in water:

$$HNO_{3(aq)} + H_2O_{(l)} \longrightarrow H_3O^{+1} + NO_3^{-1}{}_{(aq)}$$

Nitrous acid and sulphurous acid are both weak acids and therefore only partially ionize in water:

$$HNO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^{+1} + NO_2^{-1}{}_{(aq)}$$

Due to super smoke stacks sending pollutants high into the atmosphere and wind carrying them, they will wind up all over North America where they will combine with water to produce acid rain far away from the source of the pollutants.

Removing sulphur from gasoline would reduce the production of sulphurous, $H_2SO_{3(aq)}$ and sulphuric acid, $H_2SO_{4(aq)}$.

If exhaust gases from burning oil, natural gas, and gasoline were reacted with a base, e.g. $CaCO_3$, then the oxides of sulphur could also be removed:

$$CaCO_3 + H_2SO_{4(aq)} \longrightarrow CaSO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$$

This, however replaces the oxides of sulphur with oxides of carbon which also causes the formation of the weak carbonic acid, $H_2CO_{3(aq)}$. However carbonic acid is a much weaker acid than $H_2SO_{3(aq)}$ and $H_2SO_{4(aq)}$, and thus minimizes the effect of acid deposition in the environment

Effects of Acid Deposition on the Environment

1. Acid rain corrodes buildings and statues and monuments, (building materials are generally calcium carbonate).
Both dry deposition and acid rain react with metals such as iron to form salts thus leading to corrosion of metallic structure as bridges, railroad tracks and vehicles.

2. Acid rain effects the growth of plants (leaves, germination of seeds, growth of vegetables).
Important minerals such as Mg^{+2}, Ca^{+2}, and K^{+1} present in the soil become soluble and are washed away in a process caused *leaching*, before they can be absorbed by plants.
Further acid rain causes the release of other ions such as Al^{+3}, which damages plant roots.

3. Acid rain destroys plants and animals in lakes (growth cycles, respiration in fish, plant tissue).
Many fish can not survive at pH below 5. Below pH 4, rivers become dead because toxic Al^{+3} ions normally present in rocks as insoluble aluminium hydroxide leach out due to the acidity of the water:

$$Al(OH)_{3\,(s)} + 3H^{+1}_{(aq)} \longrightarrow Al^{+3}_{(aq)} + 3\,H_2O_{(l)}$$

Aluminium ions interfere with the operation of fish's gills and reduce their ability to take in oxygen.

4. Acid rain causes leaching of heavy metals (Hg, Al, Cd, Cu ....) into the drinking water.

Other Pollutants

Principal pollutants in the atmosphere

Pollutant	Principal Source	Effects
Hydrocarbons	gasoline combustion	smog, respiratory disease
carbon monoxide	incomplete combustion of gasoline	toxicity
chlorofluorcarbons (CFC)	refrigeration, aerosol sprays, plastic manufacture	destruction of ozone layer
polychlorophenols (PCB)	utility poles	aquatic plants and animals
organochlorides: dioxins and furans	incinerators	cancers
Dust	mines, industries, cities	respiratory disease
radioactive fallout	nuclear reactors, nuclear energy experimentation	mutations, cancer
carbon dioxide	fossil fuels, plants	contributes to greenhouse effect

Principal pollutants in the aquatic environment

Pollutant	Principal Source	Effects
Hydrocarbons (petroleum, benzene)	industries, transport, organic solvents	destruction of aquatic fauna, polluted water
human waste and oils	industries, municipal sewage, gasoline	pollution of potable water, bacterial and viral disease
inorganic material (acids, bases, salts, metals)	industries, mines, municipal sewage	corrosion, toxicity
Fertilizers (nitrate, phosphates)	agriculture, industries	toxicity
Pesticides, herbicides	agriculture, forestry	cancers, toxicity, disruption on food chain

Responses to acid deposition

1. Reduction of SO_2 emissions:

i. Pre-combustion methods: processes to remove the sulphur present in coal, oil before combustion

ii. Post-combustion methods; removal of SO_2 from flue gas in the smoke stacks of coal -power stations before release into the atmosphere.

2. Reduction of NO_X emissions

i. Catalytic converters in vehicles

ii. Lower temperature combustion: recirculating the exhaust gases back into the engine lowers the temperature to reduce the nitrogen oxide in the emissions.