

ENVIRONMENTAL REACTION ENGINEERING

1.1 Introduction

Chemical reactions play a key role in generation of pollutants (e.g. combustion of fossil fuels) as well as in pollution abatement (e.g. automobile exhaust catalytic converter). Hence, the understanding of reaction systems, is necessary in environmentally conscious manufacturing, in "end of the pipe treatment" of pollutants, "in-situ" pollution remediation and in modeling global effects of pollutants. Quantitative understanding of chemical reactions rests on two cornerstones of physical chemistry: chemical thermodynamics and chemical kinetics. The principles of thermodynamics define composition at equilibrium, i.e. the condition towards which every closed system will tend. Chemical kinetics quantifies the rate at which equilibrium is approached. Both thermodynamic and kinetic concepts are needed for a full quantification of pollution generation and abatement since rate processes are often dominant over thermodynamic considerations. Prediction of air quality and water quality, as well as the quantification of the effects induced by humans, and of the natural processes, on the whole ecosystem, also require good understanding of reaction systems. In addition to being able to predict how far a reaction can proceed and at what rate, it is also important, when dealing with pollution prevention and remediation, to be able to assess the effect of physical transport processes (e.g. diffusion, heat transfer, etc.) on the reaction rate and "engineer a reaction system" in a desirable way. The study of reaction rates and engineering of reaction systems pertinent to environmental control or remediation, is the subject of this set of notes. Since this text is meant for students in science and engineering of diverse backgrounds who are interested in the environment, we will start with the most fundamental concepts first and attempt to explain them in the simplest terms. Then we extend these concepts and illustrate their use in engineering practice. MATLAB based simulation tools are also provided to facilitate learning the concepts.

Understanding chemical, photochemical, biochemical, biological, electrochemical and other reactions and their kinetic rates and the rates of associated physical transport processes, is important in reaction systems involved in:

- pollution generation in chemical processes;
- pollution abatement via end of the pipe treatment;
- waste water treatment;
- fate of pollutants in the environment;
- pollutant dynamics in the atmosphere;
- pollutant dynamics in aquatic systems;
- global and regional pollutant dynamics.

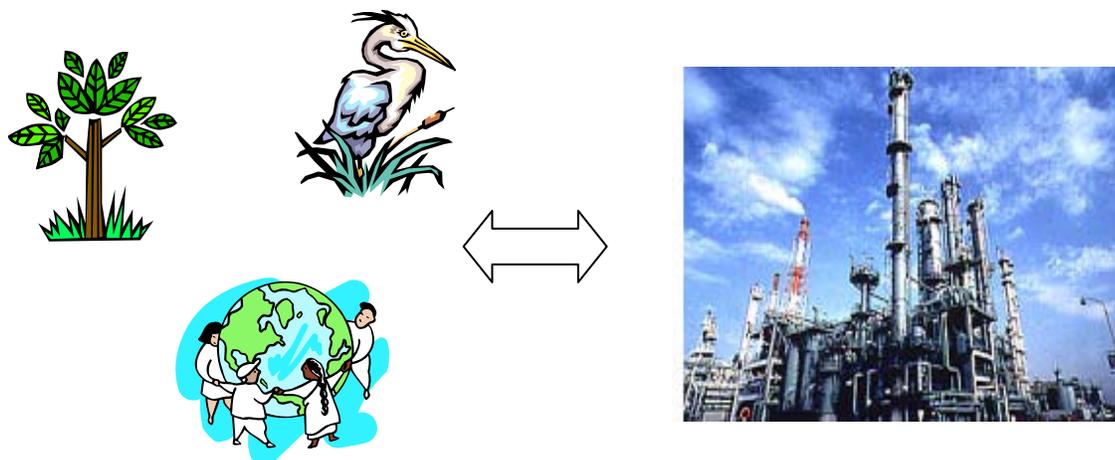


Figure 1: Chemical Manufacturing and the Environment

The scope of this chapter is to introduce the pertinent chemistry involved in some of these processes and provide a perspective on the knowledge base needed to do some of these studies.

1.2 Reactions leading to generation of pollutants

There are several sources of pollution: Carbon monoxide and nitrogen oxides emitted as exhaust from cars, SO_2 released in power plant flue gases, emissions from the chemical industry, etc. Figure 2 gives a simplified schematic for the pollution cycle.

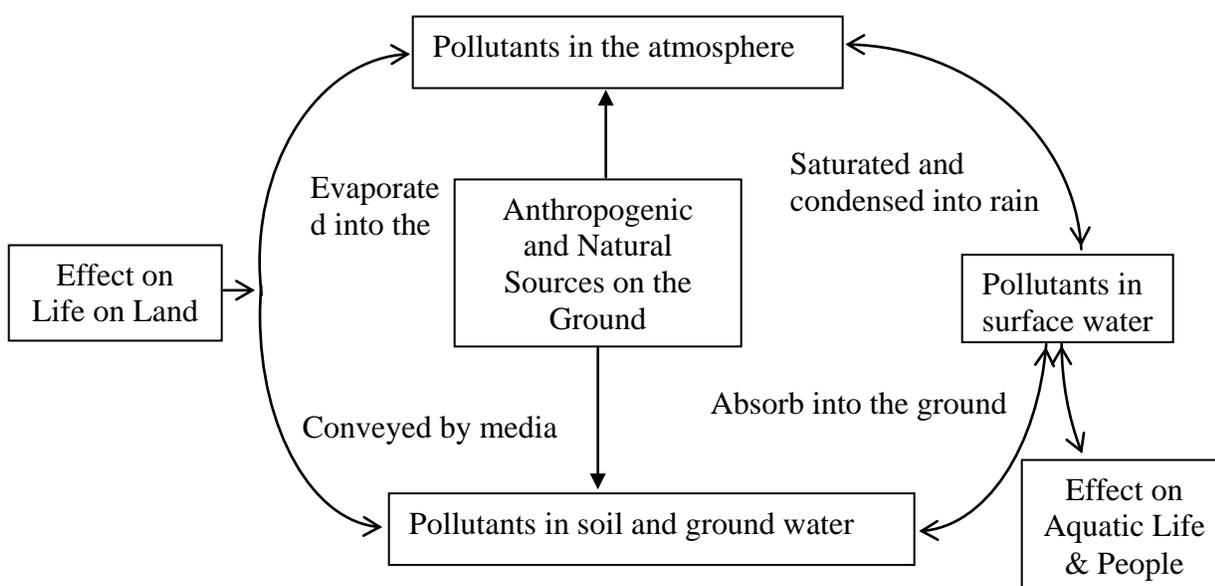


Figure 2: The cycle of pollution

1.3 Impact of Pollutant and Their Reactions on the Environment

In this section, we introduce examples of the impact of pollutants in the environment. In particular, we focus on ozone depletion, smog formation and acid rain. Let's start with ozone depletion.

1.3.1 Ozone Depletion

In general, the concentration in the atmosphere of gases such as CH_4 , CO , CO_2 , NO_x , and SO_2 has increased over this century. The reason for this is a cumulative effect of fossil fuels combustion, in particular automobile and power plant exhaust gases, and of other human activities such as farming, deforestation, increased biomass activity due to landfills, etc. The chemical industry also contributes to the atmospheric pollution, but is not the sole culprit.

Gases, which are relatively insoluble and unreactive readily spread through the troposphere (lower 10-15 km of earth) and in some cases, find their way to the stratosphere (10-50 km above the surface). Figure 3 gives a schematic of atmospheric reactions in the troposphere and stratosphere.

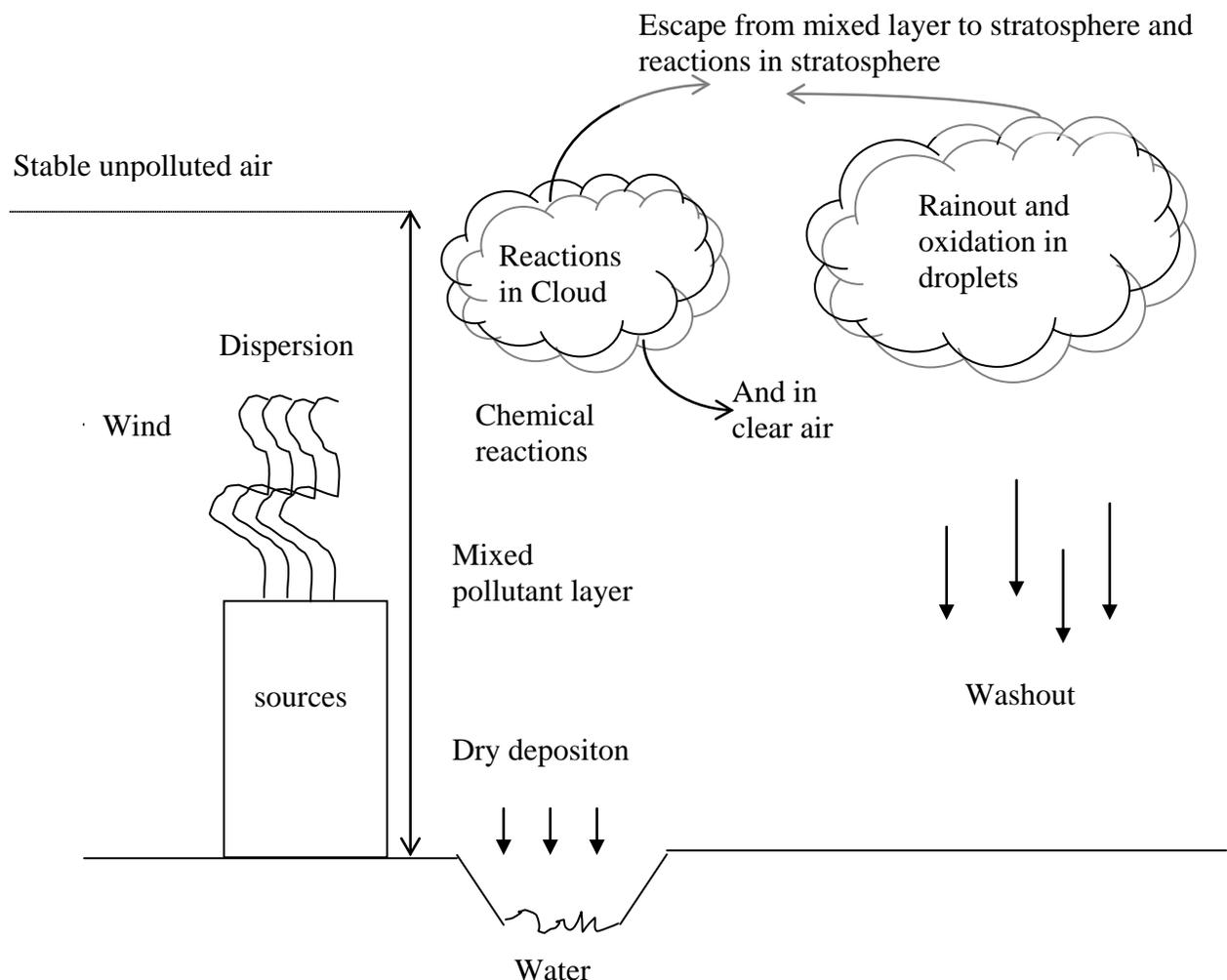
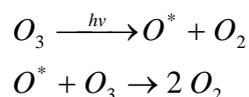


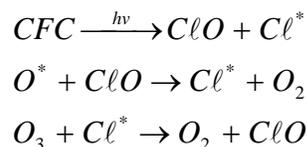
Figure 2. Spreading and reactions of pollutants in troposphere and stratosphere.

It is important to note that ozone can be “good” or “bad” depending on where it is in the atmosphere. The “good” ozone shields the earth’s surface from intense ultraviolet radiation and is located in the stratosphere. The chlorine atoms released from CFC (chlorofluorocarbons) play a critical role in the destruction of the protective ozone layer.

In the stratosphere UV radiation is intercepted by ozone which then decomposes naturally into oxygen by a simple mechanism.



The rate of this natural decomposition of ozone is much enhanced by the presence of chlorofluorocarbons (CFC) as follows:

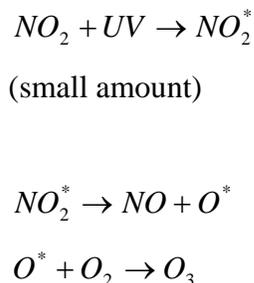


This catalytic cycle by which ClO is continuously regenerated enhances ozone decomposition almost 200 times at temperatures of around 200K in the stratosphere. In this course we will be learning how to deal with mechanisms in deriving the rates of reaction and how to estimate these rates.

The ozone depletion is a great concern since ultraviolet radiation can be very harmful to crops, trees, animals and people.

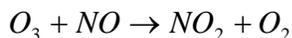
The “bad” ozone is located in the troposphere and is produced photolytically with help from nitrogen oxides as can be seen from the following reaction scheme.

Photolytic production of ozone:



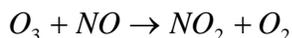
The ozone produced then reacts with nitrogen oxides and hydrocarbons resulting in smog creating aldehydes and other oxidation products.

Reactions of ozone:



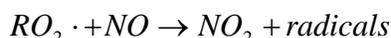
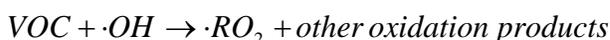
1.1.1 Smog Formation

Photodissociation of NO_2 is responsible for lower atmosphere ozone formation. NO formed combines back with O_3 keeping a steady state level for O_3 .



Thus, our acceptable level of O_3 is maintained in the absence of atmospheric pollutants such as VOC or excessive nitrogen oxide concentration (we will see later that ozone “tracks” NO_2/NO ratio).

The role of Volatile Organic Compounds (VOCs) is to form radicals that convert NO to NO_2 , without the need for ozone, as can be seen in the following reaction scheme.



As the concentration of VOC increases, NO_2/NO ratio and ground level “bad” ozone levels also increase. The increased ozone formation leads to the following reaction



leading to smog formation.

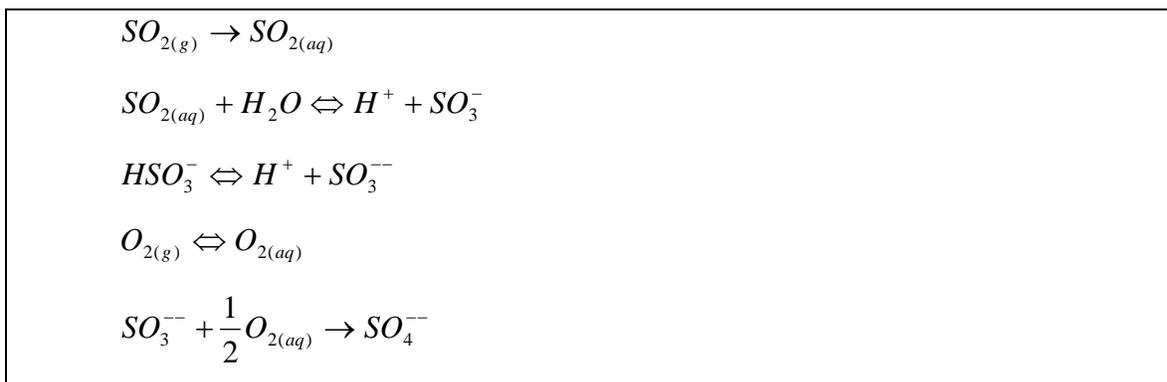
The rate constant for the formation of hydroxyl radical is a measure of smog formation potential. Estimation methods for the rate constants will be reviewed later. Incremental reactivity scale is a measure of contribution of various groups to the rate of VOC reaction with OH° radicals and is often used a measure of smog formation potential of any particular chemical. The formal definition of incremental

reactivity is the change in moles of ozone formed as a result of emission into air-shed of one mole (on a carbon atom basis) of the VOC. Such considerations are important in assessing the environmental impact of any chemical being used in, for example, consumer products. It may also be noted that OH° radicals are normally present in the atmosphere to facilitate the reaction with VOCs. The concentration is very small but significant enough to cause smog.

1.1.2 Acid Rain

Rain water is supposed to be pure of distilled water-like quality but gets contaminated by interaction with pollutants in the air. Best known examples of such contaminations are acids generated from NO_x and SO_x emissions. The distribution of these and other pollutants (once they are released into the atmosphere) depends on gas-liquid equilibrium: partition or solubility coefficient. Thus, the pollutants seek out and concentrate in the medium in which they are most soluble. The insoluble gases may react with other components present in the air environment. Soluble gases such as SO_2 , released as part of flue gases, are absorbed in water droplets (rain, snow, fog or dew) rain. Dissolved SO_2 in water droplets reacts to form SO_3 and subsequently H_2SO_4 . These SO_2 conversion reactions are schematically represented in Table 1 and result in acid rain.

Table 1. Reactions of SO_2 in the environment



Acid rain is thus formed predominantly by the oxides of sulfur and nitrogen. The later also catalyze sulfuric acid formation. The basic sources of sulfur dioxide and nitrogen oxides are indicated below:

Sulfur dioxide (SO_2) in the atmosphere results from:

- oxidation in the course of combustion of fossil fuels
- former “Kraft” process for paper manufacture
- natural emissions of biological origin such as dimethyl sulphide and hydrogen sulphide
- physical coal cleaning (PCC) plants
- fluid catalytic cracking: (FCC) off gases

Nitrogen oxides (NO_x) in the atmosphere come from:

- process of combustion by oxidation of nitrogen present in the air: the degree to which this occurs is dependent on the combustion temperature (high temperature promotes it).
- nitrogen content of the combusted materials (e.g. organic waste)
- nitric acid plant emissions

An indirect effect of acid rain, positive ion leaching out of soil can be harmful to fish in rivers and lakes. Ammonia can also enter water from the atmosphere. The surface water gets contaminated by traditional organic wastes as well as from industrial wastes.

The groundwater is contaminated by pollutants leaching through the soil. Normally, biodegradation is a natural cleaning process which is always in action. The extent to which a hazardous waste can be biodegraded depends on its half-life. Groundwater contamination is less reversible since the aerobic microbes are not present to the extent they are found in lakes and rivers.

1.3. Chemical Reactions in Major Treatment Technologies

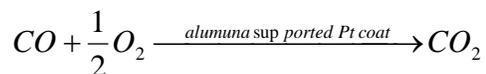
In this section, we discuss briefly chemical reactions in the pollutant removal processes with examples of multiphase systems, which are prevalent, and provide initial guidelines for green engineering and processing. Among multiphase systems, we mention here Gas-Solid and Gas-Liquid Catalytic Reactions.

1.3.1 Gas Solid Catalytic Reactions

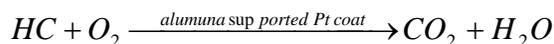
1. Automobile Emission Control

Catalytic converter is an anti-pollution device located between a vehicle’s engine and tailpipe. It is used to control the exhaust emission and reduce the high concentrations of hydrocarbons and carbon monoxide. Catalytic converters work by facilitating chemical reactions that convert exhaust pollutants, such as carbon monoxide and nitrogen oxides to normal atmospheric gases such as nitrogen, carbon

dioxide and water. The pollutants are reduced by contacting them with oxygen over a solid catalyst; usually an alumina supported Pt catalyst.



or



Various types of reactors can be used and the choice will be discussed in a later chapter.

2. Catalytic Oxidation of VOCs

VOCs are a common source of pollutants present in many industrial process stack gas streams and include a variety of compounds, depending on the process industry. The catalytic oxidation removes the pollutant at $T < T_{incineration}$, thus the capital costs are lower than that of thermal oxidation. The operating temperatures are between 600F to 1200F. That is around 315 to 650°C. Catalysts are bonded to ceramic honeycomb blocks so that the pressure drop through the catalytic reactor can be kept low. Design of these systems and the cost of treatment will be studied in a later chapter.

3. Incineration

Incineration, or afterburning, is a combustion process used as thermal oxidizer to remove combustible air pollutants (gases, vapors and odors) by oxidizing them. Complete oxidation of organic species results in CO_2 and H_2O . Reduced inorganic species are converted to an oxidized species, e.g. the conversion of H_2S to SO_2 . The presence of inorganic species, such as Cl, N, and S, in the waste stream can result in the production of acid gases after the incineration process. These acid gases, if present in high enough concentration, need to be scrubbed from the air-stream before being emitted to the atmosphere.

There are two basic types of incinerators:

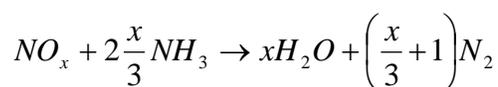
Direct thermal: heated above the ignition temperature and held for a certain length of time to ensure complete combustion. (generally between 650 to 820 °C (1200-1500°F) for 0.3-0.5 seconds)

Catalytic thermal: use of lower temperature (320 to 400°C i.e. 600-750°F) at the catalyst inlet) than the direct thermal incinerators for complete combustion, and therefore use less fuel and are made of lighter construction materials.

Again the choice of technology is a balance of conflicting factors. Note that the lower fuel cost may be offset by the added cost of catalysts and the higher maintenance requirements for catalytic units. As a general rule, direct thermal units operating above (750°) achieve higher destruction efficiencies than catalytic thermal units.

4. Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) refers to reduction of a nitrous oxide to nitrogen by reacting it with ammonia in presence of a solid catalyst. Both anhydrous and aqueous ammonia have been used in actual applications.



This technology is used for example in treating flue gases from large scale boilers.

1.3.2 Gas Liquid Reactions

Absorption is a widely used unit operation for transferring one or more gas phase inorganic species into a liquid. Absorption of a gaseous component by a liquid occurs because the liquid is not in equilibrium with the gaseous species. This difference between the actual concentration and the equilibrium concentration provides the driving force for absorption. Absorption can be physical or chemical. Several types of absorbers are used in practice, the packed tower absorber being one of the most common. Some examples are as follows:

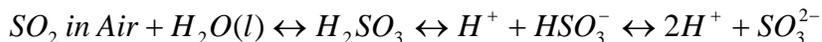
1. FCC Off-Gas Cleaning

FCC (Fluid Catalytic Cracking) off-gas from the catalyst regenerator is a major source of pollutants in oil refineries. These gases contain SO_x (quantity depends on the sulfur content of feed) and NO_x. These gases are treated in a spray column. The spray is water with additives such as alkali, caustic soda or lime. The properly designed spray column also removes particulate matter present in the off-gas as well as NO_x. The pressure drop is low due to the open design of the column with few internals.

2. Wet Gas Scrubbing

This process is useful for removal of highly diluted SO₂ from flue gases. The process uses a concentrated sodium sulfite solution. The absorbed SO₂ is thermally released in a concentrated form from the bisulfite solution in an evaporator/crystallizer.

Physical absorption occurs when a soluble gaseous species, e.g. SO₂, dissolves in the liquid phase, e.g. water. In the case of SO₂ absorbing into water, the overall physical absorption mechanism is



Chemical absorption occurs when a chemical reaction takes place in the liquid phase to form a new species. In the case of SO₂ absorbing into water containing calcium, the overall absorption mechanism is



The absorbed SO₂ (in the form of bisulfite) is thermally released in an evaporator (crystallizer).

SO₂ emerges as a concentrated gas containing 95% SO₂ by volume. This can be converted to elemental sulfur, liquid SO₂ or sulfuric acid.

3. H₂S removal and spent caustic oxidation

Caustic solutions are often used to treat H₂S and mercaptanes contained in gas streams. The sulfides are formed as a result of reaction with caustic solution with the sulfur bearing compounds. This waste stream is highly toxic with high chemical oxygen demand (COD). Hence, the caustic solution has to be oxidized to form thiosulfate/sulfate. The treated stream is then suitable for wastewater treatment unit.

In this chapter, we looked briefly at some reactions leading to pollution. We also consider a few methods that can be used in treatment. These treatment methods are multiphase in nature. Much research has been devoted to investigate the type of reactors that can be employed for multiphase systems and how these reactors can be improved to get better treatment. It is the purpose of this book to illustrate the principles of reaction engineering in terms of reactor design in environmental applications. In the next chapter, we will start by reviewing thermodynamic principles and applications. We will then proceed with reaction mechanisms and kinetics. We will then show how to model reaction systems. Applications to atmospheric system will be shown. Then we proceed to introduce basic reactor design models and illustrate their applications in pollution abatement and treatment.

