SOURCES OF AIR POLLUTION

The composition of dry air in the atmosphere contains, in addition to major constituents nitrogen and oxygen, minor and trace level constituents. Air is considered to be polluted when it contains certain substances in concentrations high enough and for duration long enough to cause harm or undesirable effects. Air pollution is defined as the presence in the atmosphere of air contaminants in such quantities and duration that they may tend to be injurious to life, or property, or they may interfere with the comfortable enjoyment of life or property, health, repose and safety. These

contaminants include gases, fumes, vapours, aerosols, and liquids and particulate matter. Troposph
is the region where weather and air pollution arises.

There has always been a balance between natural sources and sinks to air pollution, but hum
and industrial activities have created pollution problems that overburden the natural remo
systems for pollutants. The places from which pollutants emanate are called 'sources', and destinatic
to which pollutants reach are called 'sinks' (soil, vegetation, etc.). Receptors are inanimate as w
as animate bodies that receive and are seriously affected by pollutants.

Sources of air pollution are natural as well as man-made. Natural sources are volcano
forest fires and dust storms. Man-made sources are industrial, metallurgical, manufacturing a
utility establishments. Most of the anthropogenic atmospheric pollutants originate from combustic
processes. The mechanisms whereby pollutants are removed from the atmosphere are call
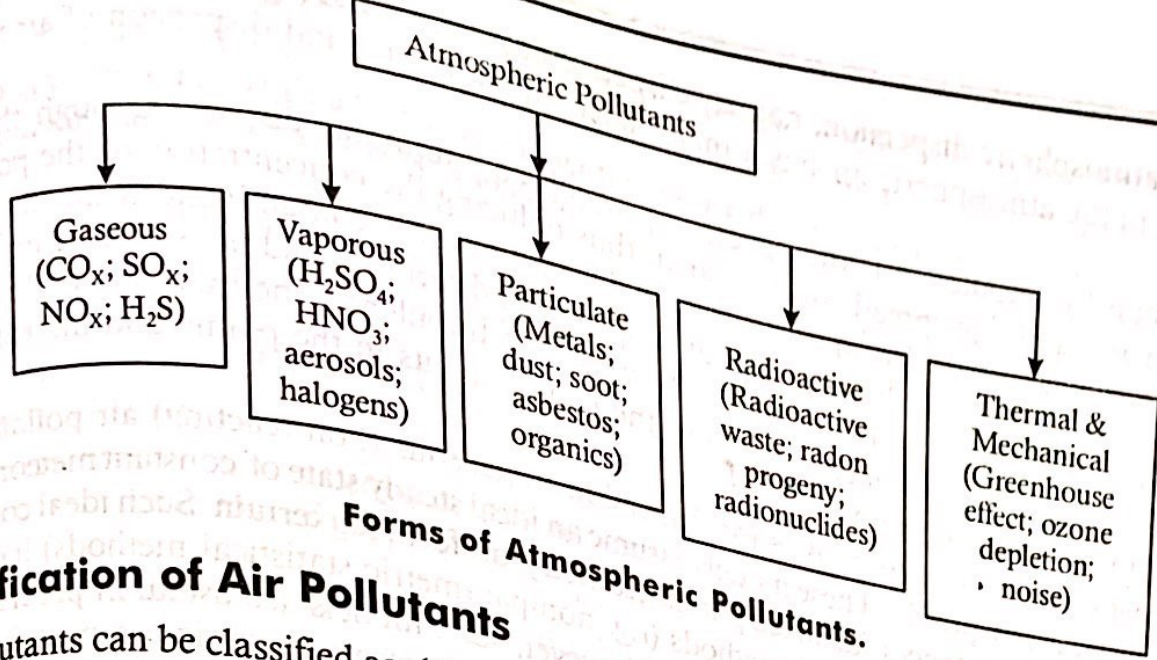'scavenging' processes. Oxidation is a prime removal mechanism for inorganic as well as organ
gases.

Air pollution problem has local, regional, continental and global ramifications. Local lev
pollution affects at the local, municipal, town and city levels; regional level pollution affects at t
troposphere level and continental pollution at the stratosphere level. Global level pollution affec
the entire atmosphere. Sources causing pollution at different levels are different.

1. **Local Level Pollution.** Local agricultural activities, waste, sewage disposal and other utilit
    and service establishments.
2. **Regional Level Pollution.** Power plants and large-scale industries.
3. **Continental Level Pollution.** Acid rain.
4. **Global Level Pollution.** Air transport, atmospheric testing of nuclear weapons, depletion
    of ozone layer, global warming due to "greenhouse" effect, reduction of solar flux reaching
    the earth due to contaminants in the atmosphere.

Air pollution sources are either site-specific, such as industrial power plants, waste disposable
units, residential, occupational and recreational places, or diffuse or mobile sources, such as
agriculture, forestry, mining, and vehicular and other transport systems.

Air pollutants from the atmosphere reach the surface of the earth by sedimentation, washout or
impaction. If the pollutant is soluble in water, it can enter the food chain directly through or via
aquatic organisms. If the pollutant is not soluble in water, it may settle on plant leaves and fruits
and thus may enter the food chain.

Pollutants can originate from point, non-point (diffuse) and mobile sources. Stationary objects,
which release pollutants, are classified as point sources (e.g. factories, smokestacks). Since bulk of
the anthropogenic pollutants, both criteria and hazardous types result from industrial activity, the
power plants (thermal and nuclear), and oil refineries, metallurgical and chemical industries and
refuse incinerating plants fall in this category. Volcanic eruptions release large quantities of particulate
matter of complex chemical composition, oxides of sulfur and compounds of fluorine. Therefore,
among the major sources of natural pollution volcanoes are also included in this category. Non-
point diffusion sources are residential areas, hospitals, utility and waste-disposal units, forestry
(forest fires) and agriculture operations. The mobile sources are a special category of non-point
emitters. Transport vehicles using coal, diesel or gasoline, contribute a major part of modern day
pollutants. Cars and trucks are considered on-road mobile sources. Tractors, lawn-movers, boats,
ships, locomotives and airplanes are off-road mobile sources. The major pollutants produced by
these sources are hydrocarbons, SO_x, NO_x, CO_x and smoke.

Atmospheric Pollutants

Gaseous (CO_X; SO_X; NO_X; H_2S)

Vaporous (H_2SO_4; HNO_3; aerosols; halogens)

Particulate (Metals; dust; soot; asbestos; organics)

Radioactive (Radioactive waste; radon progeny; radionuclides)

Thermal & Mechanical (Greenhouse effect; ozone depletion; noise)

Forms of Atmospheric Pollutants.

Classification of Air Pollutants

Air pollutants can be classified as: (1) primary and (2) secondary types. Primary air pollutants are substances that exist in the same form, such as CO, CO_2, SO_2, H_2S and metal vapours, as in source emissions and which are released directly into the atmosphere from the source industries or operations. A large number of hazardous chemicals are also released directly. Secondary pollutants are produced in the atmosphere by interaction between various substances present there or as a result of chemical reactions. Ozone, smog and components of acid rain (H_2SO_4 and HNO_3) are examples of secondary pollutants. The distinction between the two types is important while dealing with their attenuation. Some common secondary pollutants are given in given table.

Typical Secondary Pollutants.

Primary Pollutants	Secondary Pollutants	Type of Reaction
Acid + Alkali	Salt	
$SO_2 + H_2O$	H_2SO_4	Acid-Base Reaction
$NH_3 + SO_2$	$(NH_4)_2SO_4$	Oxidation
$NO + O_2$	NO_2	Oxidation
$NO + O_2 + HC*$	O_3 + Free radicals	Photochemical
		Photochemical

*HC = Hydrocarbons

Transport and Diffusion of Pollutants

The goal of air quality dispersion modeling is to estimate a pollutant's concentration at a point downwind of one or more emission sources. The dispersion models are useful tools for detecting potential concentration impacts from sources. The plume rises mainly due to two factors: (1) the velocity of exhaust gases, which impart momentum to the plume, and (2) the temperature of the exhaust gas, which gives the plume buoyancy in ambient air. Some meteorological factors that affect plume rise include wind speed, air temperature, atmospheric stability, and turbulence and land topography. The plume models are empirical mathematical models aimed at obtaining a first estimate of plume concentrations of non-reacting atmospheric pollutants. Friction effects and chemical reactions are neglected in the plume models.

The heat transfer by simple diffusion is by conduction, but the process of dispersion is by convection (by turbulence). Therefore, the Fick's laws of diffusion cannot adequately explain the dominant

process in atmospheric dispersion, namely ~~dispersion by~~ (turbulence). The amount of turbulence in the atmospheric air has a major effect upon the rise and dispersion of air pollutant plumes.

Dispersion by turbulence is the process by which contaminants disperse through the air by convection and a plume spreads over an area, thus reducing the concentration of the pollutant. The plume spreads vertically and horizontally. Dispersion of a contaminant in the atmosphere depends on wind speed, turbulence and atmospheric and terrain conditions. Turbulence mixes and enhances the dispersion of pollutants. Stronger the turbulence, the more the pollutants are dispersed. It decreases the concentrations of the contaminants in the plume and increases their concentrations outside the plume.

The most commonly used models for dispersion of gaseous (non-reacting) air pollutants are based on the Gaussian profile. These models assume an ideal steady state of constant meteorological conditions over long distances, idealized plume geometry, uniform flat terrain. Such ideal conditions rarely occur. More robust statistical methods (e.g. non-parametric statistical methods) have to be applied in addressing such multivariate cases. However, such models are useful in predicting the dispersion and dilution of stack gases, and atmospheric pollutants under various atmospheric and terrain conditions.

The concentration of a pollutant, $\dot{C}_x$, at a distance, X, from the source is

$$C_x = \frac{Q}{\pi U \sigma_y \sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2}\right)$$

where, Q = source strength;
σ = standard deviations in x, y and z direction;
U = average wind speed

Concentration can be correlated to diffusion coefficients, which gives an estimate of the spread of the pollutants horizontally (along wind direction), laterally and vertically.

$$C = \frac{Q}{4\pi r} \frac{1}{\sqrt{(D_y D_z)}} \exp\left[\left(-\frac{U}{4x}\right)\left(\frac{y^2}{D_y} + \frac{z^2}{D_z}\right)\right]$$

where, $r = \sqrt{(x^2 + y^2 + z^2)}$; D_y and D_z are diffusion coefficients in the lateral and vertical wind directions.

In the case of stable atmosphere (inversion), the stability parameter, S, is given by

$$S = \frac{\Delta g}{T}\left(\frac{dT}{dz} + \tau\right)$$

where, $\tau = \left(\frac{dT}{dz}\right)_{adiabatic}$

For an adiabatic ambient (neutral) atmosphere, $\frac{dT}{dz} = -\tau$; and $S = 0$

For stable atmosphere, $\frac{dT}{dz} > \tau$; and $S > 0$

For unstable atmosphere, $\frac{dT}{dz} < \tau$; and $S < 0$

Gas Laws Governing the Behviours of Pollutants in the Atmosphere

Air pollution modeling (Gaussian and other) procedures address the concentration dispersion of non-reacting pollutants. While dealing with reacting pollutants, principles of both thermodynamics and reaction kinetics have to be invoked to study the rate of formation and distribution of reacting pollutants.

Endothermic reactions are more complete at higher temperatures. For example, in combustion the dissociation of CO_2 is temperature-dependent and occurs only above 2,000° C, but NO_x pollutants are produced at higher temperatures.

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2 \quad \text{(endothermic; requires energy to proceed)}$$
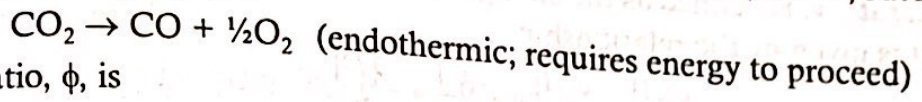
The equivalence ratio, ϕ, is

$$\phi = \frac{(\text{fuel} / \text{oxidizer})}{(\text{fuel} / \text{oxidizer})_{stoichio}}$$

$\phi > 1$ fuel-rich (air-lean).

$\phi < 1$ fuel-lean (air-rich).

The effect of ϕ, the fuel/air ratio is very important in combustion.

CO builds up for $\phi > 1$ (fuel-rich/air-lean).

NO builds up for $\phi < 1$ (fuel-lean/air-rich).

An air-rich mixture tends to produce minimal CO, but produces NO, and a fuel-rich mixture produces more CO and less NO. Keeping combustion temperature down tends to reduce both CO and NO (by reducing compression ratio in automobiles); but reduced combustion temperature and compression ratio result in reduced efficiency of the engine.
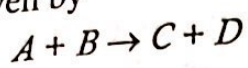
Knowledge of the reaction rates of the reacting constituents is important in understanding and controlling the chemical and biodegradation processes, and for the evaluation of the persistence of pollutants and to assessing exposure of humans and other living organisms. Knowledge of the reaction mechanisms involved may make it possible to choose reaction conditions favouring one path over another, thereby obtaining maximum amounts of desired products and minimum amounts of undesirable products i.e. pollutants. Once degradation of a chemical commences, the amount disappearing with time and the shape of the disappearance curve will be a function of the compound in question—its concentration, the organisms responsible, and a variety of environmental factors. The concentration-time relationship characterizes the concentration of the chemical remaining at any time and permits prediction of the levels likely to be present at some future time, and allows assessment of whether the chemical will be eliminated before it is transported to a site at which humans, animals and plants may be exposed.

Kinetic methods are based on relationships quantitatively describing the dynamics of reaction systems and permit determination of reaction mechanisms. This approach requires exact knowledge of the dependence of concentration of reactants as a function of time and of the reaction mechanisms. Reaction kinetics methods deal with these problems. Reaction kinetic formalisms quantitatively describe the dependence of the reaction rate on the concentrations of the components of the reaction system. Reaction rates depend on the nature and concentration of the reactants, temperature, pressure and the presence of catalysts.

The rate of reaction is proportional to the product of the concentrations of those substances that comprise the transition state. If the concentrations of all but one reactant are held constant while

the concentrations of that reactant... changes will establish how many molecules of that particular reactant are involved in the transition state. This figure is called the order of reaction with respect to the reactant in consideration.

In general, for reactants, A and B forming products C and D, in molar stoichiometric ratios, the relationship is given by

$$A + B \rightarrow C + D$$

The reaction rate, v, is defined as the change with time in the concentrations of the components in reaction and is given by the relationship

$$v = -\frac{d[A]}{dt} - \frac{d[B]}{dt} + \frac{d[C]}{dt} + \frac{d[D]}{dt}$$

But, for many simple, irreversible reactions, the reaction rate is

$$v = K[A]^\alpha [B]^\beta$$

where, α and β are reaction order with respect to substances A and B; K = rate constant

Reactions are classified according to the order of reaction ($n = \alpha + \beta$, the overall reaction order).

0th order ($n = 0$, $\alpha = 0$, $\beta = 0$): $-\dfrac{d[A]}{dt} = K$

1st order ($n = 1$, $\alpha = 1$, $\beta = 0$): $-\dfrac{d[A]}{dt} = K_A[A]$

2nd order ($n = 2$, $\alpha = 2$ (or 1), $\beta = 0$ (or 1): $-\dfrac{d[A]}{dt} = K[A]^2$ or $K[A][B]$

3rd order ($n = 2$, $\alpha = 3$ (or 2), $\beta = 0$ (or 1): $-\dfrac{d[A]}{dt} = K[A]^3$ or $K[A]^2[B]$

n^{th} order ($nn0$, $n \neq 1$): $-\dfrac{d[A]}{dt} = K[A]^n$

where, $[A]$, $[B]$, $[C]$ etc., are molar concentrations and K = rate constant.

Rate constants vary during the reaction and depend on the initial concentrations of the reactants. For a simple 2nd order reaction, the relationship between activity coefficients is given by

$$\frac{dx}{dt} = K[A][B] = K^0 \frac{\gamma_A \gamma_B}{\gamma_{(AB)^*}}[A][B]$$

where, γ_A, γ_B, $\gamma_{(AB)^*}$ are the activity coefficients of substances A and B and activated complex $(AB)^*$ respectively, K^0 = rate constant of the reaction at infinite dilution,

Where ($\gamma_A = \gamma_B = \gamma_{(AB)\#} = 1$), Therefore,

$$K = K^0 \frac{\gamma_A \gamma_B}{\gamma_{(AB)^*}}$$

The rate of chemical reaction is temperature dependent. It can be increased by an increase in the temperature of the reaction mixture. The dependence of the rate constant on the temperature is given by the Arrhenius equation, which is related to entropy and enthalpy factors.

$$K = F \exp\left(-\frac{E^*}{RT}\right)$$

$$K = \frac{k_B}{h} \exp\left(\frac{\Delta S^*}{R}\right) \cdot \exp\left(-\frac{\Delta H^*}{RT}\right)$$

where, F = frequency factor, E^* = activation energy, R = gas constant, T = absolute temperature, k_B = Boltzmann constant, h = Planck constant, ΔS^* and ΔH^* = entropy and enthalpy of activation respectively.

Zero-order Reactions

In zero-order processes, the rate is independent of the concentration of the reactants. When the concentration is plotted against time, the concentration decreases at a constant rate in zero-order process. That is, a constant amount is lost per unit time until the entire chemical is gone. Zero-order kinetics or linear biodegradation of organic molecules has been observed frequently (e.g. mineralization of phenols, pesticides).

1st-order Reactions

In the 1st-order reactions (unimolecular reactions), the rate of reaction is proportional to the concentration of only one of the reactants.

$$aA + bB \rightarrow \text{Products,}$$
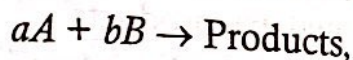
where $\quad -\dfrac{d[A]}{dt} = K_A[A];$ $\qquad \dfrac{dA}{[A]} = -K_A dt$

$\therefore \qquad [A] = [A_0]\exp(-K_A t)$

A plot of $\log[A]$ against time t, is a straight line and the slope gives the value of K_A. The concentration falls quickly initially and them more slowly in 1st-order processes. That is, a constant percentage of the chemical disappears per unit time in 1st-order reactions.

where, A_0 = initial concentration;

K_A = rate constant (not equilibrium constant).

1st-order kinetics is sometimes termed half-life kinetics because half of the chemical is degraded in time t. For 1st-order reactions, the rate constant and half-life, $t_{1/2}$ are inversely related.

$$t_{1/2} = \frac{0.693}{K}$$

A substrate whose destruction follows 1st-order kinetics persists long after the first half-life is over (e.g. metabolism of glucose by bacteria; radioactive decay).

2nd-order Reactions

In 2nd-order reactions, the rate of reaction is proportional to the 2nd power of concentration.

$$aA + bB \rightarrow \text{Products,}$$
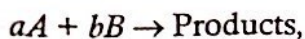
where, $\quad -\dfrac{d[A]}{dt} = K_A[A][B]$

2nd-order kinetic reactions are relevant in dealing with the reaction kinetics in catalytic and combustion reactions. Concerted bimolecular elimination reactions are characterized by 2nd-order kinetics with powerful nucleophiles.

Catalytic reactions are often systems of two successive reactions. In the first step the catalyst reacts with one of the reactants with formation of an intermediate complex.

$$C + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} M$$

$$M + R \xrightarrow{K_2} P + C$$
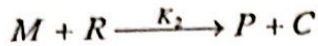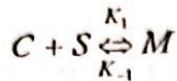
where, C = catalyst,

S = substrate,

M = intermediate complex,

R = reactant,

K_1, K_{-1} and K_2 = rate constants

For combustion reactions, the reaction sequence is

Reactants → Combustion → Intermediary product (M) → Products (P)

Reaction kinetic processes can be addressed in three steps:

1. **Initiation step.** Production of species as radicals gives rise to further reaction.
2. **Propagation step.** Chain reactions resulting in intermediary products.
3. **Termination step.** Removal of radicals and production of final products.
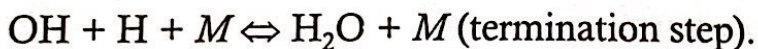
Formation of H_2O can be considered as an example: $2H_2 + O_2 \rightarrow 2H_2O$

$M + H_2 \rightarrow 2H + M$ (initiation step)

where M is energy absorber, but chemically not affected.

$H + O_2 \rightleftharpoons OH + O^*$

$O^* + H_2 \rightleftharpoons OH + H$ (chain-reaction step)

$OH + H_2 \rightleftharpoons H_2O + H$
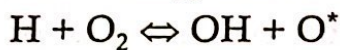
where, H is both a reactant and a product, leading to a chain reaction.

$OH + H + M \rightleftharpoons H_2O + M$ (termination step).

In the termination step, radicals, OH and H are removed.

Under such conditions, where the intermediate product is a component of the reaction process, the reaction kinetics is

$$A \underset{K-1}{\overset{K_1}{\rightleftharpoons}} M + C$$

$$M + B \xrightarrow{K_2} \text{Products}$$
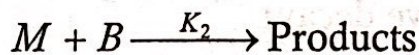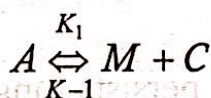
Molar concentration [M] and reaction rate are given by

$$[M] = \frac{K_1[A]}{K_{-1}[C] + K_2[B]}$$

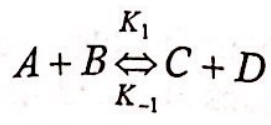$$\text{Rate} = \frac{K_1 K_2 [A][B]}{K_{-1}[C] + K_2[B]}$$

Case 1: If $K_{-1}[C] \gg K_2[B]$

$$\text{Rate} = \frac{K_1 K_2 [A][B]}{K_{-1}[C]}$$

$$\text{Rate} = K_1[A] \qquad \text{1st order reaction}$$

3rd-order Reactions

In 3rd-order the rate of reaction is proportional to the 3rd power of concentration; and products of a reaction can react to produce the original reactants.

$$A + B \underset{K_{-1}}{\overset{K_1}{\Leftrightarrow}} C + D$$

$$-\frac{d[A]}{dt} = K_1[A][B] - K_{-1}[C][D]$$

That is, a decrease in $[A]$ depends on both the forward and backward reactions. At equilibrium, the reaction is 2nd-order overall and 1st-order with respect to each concentration. At equilibrium
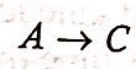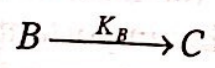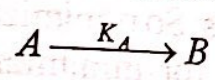
$$\frac{d[A]}{dt} = 0$$

$$\therefore \quad K_1[A][B] = K_{-1}[C][D]$$

The equilibrium constant $K(T)$ is

$$K(T) = \frac{[C][D]}{[A][B]} = \frac{K_1}{K_{-1}}$$

This relationship is used to determine one of the reaction constants, if the other is known—

$$A \xrightarrow{K_A} B$$
$$B \xrightarrow{K_B} C$$
$$A \rightarrow C$$

where, B is the product of the 1st reaction and is a reactant in the 2nd reaction and the overall reaction is $A \rightarrow C$.

$$\frac{d[A]}{dt} = -K_A[A]$$

$$\frac{d[B]}{dt} = -K_A[A] - K_B[B]$$

$$\frac{d[C]}{dt} = K_B[B]$$

$$\frac{d[A + B + C]}{dt} = 0; \qquad [A + B + C] = \text{constant}$$

$$\therefore \quad [B] = a_1 \cdot \exp(-K_B t) \qquad \text{(general)}$$
$$= a_2 \cdot \exp(-K_A t) \text{ (particular)}$$
$$[B] = a_1 \cdot \exp(-K_B t) + a_2 \cdot \exp(-K_A t)$$

Assuming at $t = 0$, both $[B] = [C] = 0$, concentration of the end product, $[C]$, can be determined from the total concentration $[A_0]$.

$$[C] = [A_0]\{1 - \exp(-K_A t)\} - \frac{\cdots}{(K_B - K_A)}\{\exp(-K_A t) - \exp(-K_b t)\}$$

$$([A_0] = [A + B + C])$$

For rate-limiting steps,

$$[C] \approx [A_0]\{1 - \exp(-K_A t) \quad \text{for } K_B \gg K_A$$
$$\approx [A_0]\{1 - \exp(-K_B t) \quad \text{for } K_A \gg K_B$$

These kinetic reaction (successive reaction) mechanisms are applicable to determine reaction rates involving molecules, ions or radicals and the rates of reactions are determined by the rates of decomposition of the intermediates (e.g. redox reactions, enzyme-catalyzed and other catalytic reactions). Applying the reaction kinetics to kinetically limited reactions (e.g. combustion processes), if a reaction is stopped before completion, all the reactant species will be present (A, B and C) and some of them are pollutants.

Understanding of combustion-generated air pollution requires an understanding of (i) stoichiometric combustion processes, (ii) the approach towards an equilibrium concentration and (iii) the effect of kinetic limitation on the final concentrations.

NO_X starts at the combustion burner.

$$K(T) = \frac{C_{NO}}{\sqrt{[C_{O_2} \cdot C_{N_2}]}}$$

where, C = concentration

$$C = C_{NO} + C_{O_2} + C_{N_2} = 1$$

Substantial amounts of NO occur only at high temperatures. So minimization of peak combustion temperature and excess of air (O_2) should be maintained for minimizing air pollution (NO_x). Residence time of N_2 in the high-temperature zone is another important control parameter. The principal factors affecting NO_x emission are thermodynamic and kinetic effects. The peak-flame temperature, the amount of excess air available and the length of time that the combustion gases are at the peak-flume temperature are the controlling parameters for NO_x production and emission. Control strategy is—(1) minimization of residence time at peak temperature, (2) reduction of the peak temperature, (3) minimization of available O_2 for reaction with N_2.