Course Name: Theory of Fire Propagation (Fire Dynamics)

Professor's Name: Dr. V. Raghavan

Department Name: Mechanical Engineering

Institute: Indian Institute of Technology Madras, Chennai – 600036

Week – 02

Lecture – 05

Module 2 – Review of thermo-chemistry, chemical equilibrium & kinetics

Stoichiometry:

Fuels contributing to fire are mixtures of saturated and unsaturated hydrocarbons, which contain some amount of C and H atoms. In many of these fuels, certain number of N, S, and O atoms are also present. Stoichiometry is the science used to determine the amount of oxidizer (air) required to completely burn one kg of the fuel to form carbon dioxide and water vapor (called major products of combustion reaction). This is a theoretical value. Air is considered to be composed of 21% oxygen and 79% nitrogen by volume, and impurities such as argon and carbon dioxide, usually present in small amounts in atmospheric air, are not considered.

For a general hydrocarbon fuel represented by C_xH_y, containing x carbon atoms and y hydrogen atoms, a global single-step reaction considering its complete combustion in air is written as,

$$\mathrm{C_xH_y} + \mathrm{a}(\mathrm{O_2} + 3.76\mathrm{N_2}) \rightarrow \mathrm{xCO_2} + \frac{\mathrm{y}}{2}\mathrm{H_2O} + 3.76\mathrm{aN_2}$$

By balancing the number of atoms on both sides, the value of a can be found as a = x + y/4. Here, nitrogen is considered as inert. The stoichiometric air-fuel ratio is calculated as the mass of air required to burn one kg of the fuel completely. It is written as,

$$\left(\frac{\mathrm{A}}{\mathrm{F}}\right)_{\mathrm{st}} = 4.76 \times \mathrm{a} \times \frac{28.84}{12 \times \mathrm{x} + \mathrm{y}}$$

Here, 4.76 is the number of moles of air, and 28.84 is its molecular mass.

Oxygen-starved and oxygen-rich burning:

When the amount of air available for combustion is less than ‘a’ kmol (oxygen-starved), species like CO, OH, H, and so on are seen in the product mixture as a result of incomplete combustion. Oxygen-starved combustion occurs in several fire scenarios occurring within compartments. In the cases of oxygen-starved combustion or when dissociation of the products occurs at high temperatures, a knowledge of the second law of thermodynamics is required to determine the possible species, which contribute to the product mixture, at a given pressure and temperature. If the air availability is higher than ‘a’ kmol, excess oxygen is seen in the product mixture. In open fires or fires burning with good ventilation, excess air entrains into the fire and the products contain excess oxygen.

Equivalence ratio, elementary reaction:

A useful parameter, called equivalence ratio, is defined as the ratio of stoichiometric air-fuel ratio to the actual air-fuel ratio. Consider a reaction with excess oxygen with dissociation of CO_2:

$$C_7H_{16} + 13.75(O_2 + 3.76N_2) \rightarrow aCO_2 + bCO + 8H_2O + cO_2 + 51.7N_2$$

Here, the equivalence ratio is 0.8. It is less than 1 for excess oxygen in the reactant and more than 1 for excess fuel in the reactant. However, products contain CO, due to dissociation of CO_2. To calculate the values of a, b, and c in the product mixture, chemical equilibrium is used. Elementary reaction for CO_2 dissociation:

$CO_2 \leftrightarrow CO + \frac{1}{2} O_2$.

This is a reversible reaction (unlike the global single-step reaction written above). At a given pressure and temperature, CO, O_2 and CO_2 will be present in some proportions.

Chemical equilibrium:

At a given pressure and temperature, a parameter called equilibrium constant, K_p, is evaluated using Gibbs free energy, defined as g = h – Ts, (h is the specific enthalpy and s is the specific entropy) and applied to the given elementary reaction:

$CO_2 \leftrightarrow CO + \frac{1}{2} O_2$.

K_p is expressed in terms of molar Gibbs free energy change (ΔG), both as a function of temperature, as well as a function of partial pressure ratio of products and reactants in a given elementary reaction. For CO_2 dissociation reaction:

$$K_p = \exp\left[\frac{-\Delta G(T, p_0)}{R_u T}\right]$$

$$K_p = \left[\frac{(p_{CO}/p_0)^1 (p_{O_2}/p_0)^{0.5}}{(p_{CO_2}/p_0)^1}\right]$$

$$\Delta G = 1 \times \bar{g}_{CO}(T, p_0) + 0.5 \times \bar{g}_{O_2}(T, p_0) - 1 \times \bar{g}_{CO_2}(T, p_0)$$

Here, p_0 is atmospheric pressure. If reaction pressure is p, then, the mole fraction of any species, $X_i = p_i/p$.

Then, $p_i/p_0 = X_i(p/p_0)$.