Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 03

Lecture – 01

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,

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

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,

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

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:

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

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

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Equilibrium products:

The unknowns, a and b in the below equation can be evaluated using carbon and oxygen balances, and the equation involving K_p.

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

$$7 = a + b$$

$$13.75 = a + (b/2) + +(8/2) + c$$

$$K_p = \exp\left[\frac{-\Delta G(T, p_0)}{R_u T}\right] = \frac{\left[X_{CO}\left(\frac{p}{p_0}\right)\right]^1 \left[X_{O_2}\left(\frac{p}{p_0}\right)\right]^{0.5}}{\left[X_{CO_2}\left(\frac{p}{p_0}\right)\right]^1} = \frac{b \times c^{0.5}}{a}\left(\frac{p}{n \times p_0}\right)^{0.5}$$

Here, n is total number of moles in products = a + b + 8 + c + 51.7

K_p is calculated using exponent term and 3 equations (set of non-linear equations) are solved to get the values of a, b and c.

Multi-component fuels:

Fire scenarios encounter fuels, which are multi-component in nature. Consider Liquefied Petroleum Gas (LPG), a fossil fuel. It is a multi-component fuel that, on an average basis, typically contains, 0.03% CH_4, 0.96% C_2H_6, 13.31% C_3H_8, 10.22% C_3H_6, 30.23% i-C_4H_{10}, 25.32% n-C_4H_{10}, 3.98% C_4H_8, 5.03% i-C_4H_8, 4.99% trans-2-C_4H_8, 3.64% cis-2-C_4H_8, 1.96% i-C_5H_{12} and 0.33% n-C_5H_{12}, by volume. It is observed here that isomers of butane such as i-butane, and that of butene, such as i-butene, trans-2- butene and cis-2-butene are present in LPG. The chemical formula for isomers is the same as normal species, but, its chemical structure varies.

Reaction with multi-component fuels:

Since volume percentages of the constituents are given, these would convert as mole percentages. Therefore, for 100 kmol of fuel, the single step reaction can be written as,

$$0.03CH_4 + 0.96C_2H_6 + 13.31C_3H_8 + 10.22C_3H_6 + (30.23+25.32)C_4H_{10} + (3.98 + 5.03 + 4.99 + 3.64)C_4H_8 + (1.96 + 0.33)C_5H_{12} + m(O_2 + 3.76N_2) \rightarrow nCO_2 + pH_2O + 3.76mN_2$$

For 1 kmol of fuel mixture,

$$0.0003CH_4 + 0.0096C_2H_6 + 0.1331C_3H_8 + 0.1022C_3H_6 + 0.5555C_4H_{10} + 0.1764C_4H_8 + 0.0229C_5H_{12} + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + 3.76aN_2$$

By atom balance, b = 3.77, c = 4.49 and a = 6.015. Molecular weight of LPG is 12×3.77 + 8.98×1 = 54.2 kg/kmol. For burning one kg of LPG theoretically, 15.23 kg of air is required.

Solid fuels:

Consider a solid fuel such as wood. Results from proximate analysis of wood give the weight percentages of its volatile, fixed carbon, moisture and ash contents. Its ultimate analysis provides the elemental composition such as percentages of C, H, O and N, on mass basis. When heated to a certain temperature, volatiles (gaseous fuels) trapped inside the wood are released. Consider a typical wood that has 80% volatiles and 20% fixed carbon from proximate analysis and 50% C, 8% H, 41.5% O and 0.5% N, obtained from its ultimate analysis, both on dry (moisture free) and ash free basis. Carbon contained in volatiles contribute to the gas-phase reactions, which are generally more rapid. Carbon in solid form burns slowly due to the reaction occurring at its surface.

Representative composition:

When the solid fuel is heated in an inert (containing no oxygen) atmosphere, volatiles are released, and fixed carbon and ash remain as solid residuals. For calculating the stoichiometric air required for gas-phase reactions involving volatiles alone, the fuel is represented in a consolidated form, $C_xH_yO_zN_p$. The moles of C, H, O and N, which are x, y, z and p, are evaluated considering results from proximate and ultimate analyses. For this calculation, molecular weight of gaseous mixture constituting the volatile matter is also required. Typical volatile species trapped in a solid fuel are CH_4, C_2H_2, C_2H_4, CO, H_2, O_2 and N_2, in some proportions, and the typical molecular weight of volatile mixture is around 30 kg/kmol.

The value of x in the consolidated fuel is calculated as,

$$\frac{\text{weight of carbon in volatile} \;/\; \text{molecular weight of carbon}}{\text{weight of volatiles in wood} \;/\; \text{molecular weight of volatiles}}$$

For this case, out of 50% C, 20% is in solid form, therefore, x is evaluated as,

$$x = \frac{(50 - 20)/12}{80/30} = 0.9375$$

Noting that hydrogen is present only in volatiles, the value of y is obtained as,

$$y = \frac{8/1}{80/30} = 3$$

Similarly, the values of z and p are obtained as,

$$z = \frac{41.5/16}{80/30} = 0.9726$$

$$p = \frac{0.5/14}{80/30} = 0.0134$$

The volatile is represented as $C_{0.94}H_{3}O_{0.97}N_{0.013}$. It is customary to rewrite this as $CH_{3.2}O_{1.03}N_{0.014}$, by keeping the number of atoms of C equal to unity.

The molecular weight of this fuel is 31.88 kg/kmol.

Further, N can be neglected and the number of atoms of H and O can be rounded off such that the fuel is represented as CH_3O. Its molecular weight is 31 kg/kmol, showing only a 2.8% reduction, which is good enough for fire analysis.

Stoichiometric reaction for volatile:

Stoichiometric reaction is written as,

$$CH_3O + 1.25(O_2 + 3.76N_2) \rightarrow CO_2 + 1.5H_2O + 4.7N_2$$

For this case, the stoichiometric air-fuel ratio for burning the volatiles is 5.535 kg/kg-volatile. It should be noted that the oxygen inherent in the fuel contributes to a notable portion for combustion. For burning unit mass of the wood (including both volatiles and fixed carbon) is calculated, the unknowns in the consolidated fuel ($C_xH_yO_zN_p$) are evaluated from the ultimate analysis only.

For the case discussed above, $x = 0.5/12$, $y = 0.08/1$, $z = 0.415/16$ and $p = 0.005/14$.

The consolidated fuel having one carbon atom and neglecting N is written as, $CH_{1.92}O_{0.63}$. The single step reaction is written as,

$$CH_{1.92}O_{0.63} + 1.165\ (O_2 + 3.76\ N_2) \rightarrow CO_2 + 0.96\ H_2O + 4.38\ N_2$$

Stoichiometric air for burning wood is 6.66 kg/kg-wood.

Heat calculations:

Heat release from a fire is an important quantity to be estimated in fire safety engineering. Fire loading is a parameter that indicates the potential hazard in case of a fire. This is calculated as the heat release flux, that is, the heat output from a fire per unit area (J/m^2). In general, if the calorific or heating value of the material (in J/kg) that is burning is known and the rate at which it is burning (in kg/s) is also known, then heat release rate is calculated as the product of these two. Calorific value is the heat released when unit mass of the material is completely burnt. Calorific values of materials used in several applications are determined by using different types of calorimeters, including the bomb calorimeter.

Heat calculation from Ist law of thermodynamics:

Theoretically, heating value is calculated using the first law of thermodynamics. For this analysis, a control (constant) volume is considered with the fire source (material that is burning) at one of its boundaries. Fuel gases from this fire source flow into the control volume. Air from the ambient also flows into the control volume and products of combustion flow out of the control volume.

Assuming steady state and steady flow, the first law is,

$$\dot{Q} - \dot{W}_x = \sum_{1}^{N} \dot{n}_i \bar{h}_i(T_P) - \sum_{1}^{M} \dot{n}_i \bar{h}_i(T_R)$$

Here, N and M are number of product and reactant species, $\dot{n}$ is flow rate in kmol/s and T is temperature in K. Subscripts P and R, represent product and reactant, respectively. Usually, $\dot{W}_x = 0$.

Heat calculation for Methane oxidation:

The term $\dot{Q}$ is the rate of heat transfer from or to the control volume, based on if it is negative or positive. The term $\bar{h}_i$ is called standard or absolute enthalpy of i_{th} species expressed in J/kmol.

For example, consider single-step reaction for methane,

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

For this reaction, the rate of heat transfer is calculated as,

$$\dot{Q} = \bar{h}_{CO_2}(T_P) + 2\bar{h}_{H_2O}(T_P) + 7.52\bar{h}_{N_2}(T_P)$$

$$-\bar{h}_{CH_4}(T_R) - 2\bar{h}_{O_2}(T_R) - 7.52\bar{h}_{N_2}(T_R)$$

Standard enthalpies of the species are calculated primarily as a function of temperature. Combustion reaction is an exothermic oxidation reaction. Hence, $\dot{Q}$ is negative.

Standard heat of reaction and standard enthalpy:

Standard heat of reaction is defined as the heat generated when reactants are supplied at 1 atm, 298 K (reference state) and the products formed are also cooled to 298 K. That is, for standard heat of reaction, the value of both T_P and T_R is 298 K.

Standard enthalpy of a species i is expressed in molar basis as,

$$\bar{h}_i(T) = \bar{h}^0_{f,i}(T_{ref}) + \Delta\bar{h}_i(T)$$

The first term on the right-hand side, $\bar{h}_{f,i}^{0}$, is called the standard enthalpy of formation in kJ/kmol. Overhead bar indicates that the enthalpy is specific to number of moles. Superscript '0' indicates that the value is obtained at 1 atmosphere pressure. It is the increase in enthalpy, when one mole of a compound is formed at constant pressure from its natural elements, in reference state and after formation, it is also brought to the reference state.