Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 02

Lecture – 06

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

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:

$CO_2 \leftrightarrow CO + ½\ O_2$.

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

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 $C_{0.94}H_3O_{0.97}N_{0.013}$. 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.