Course Name: Theory of Fire Propagation (Fire Dynamics)

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Lecture – 02

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

Standard enthalpy:

For naturally occurring elements such as O_2, H_2, N_2, C (solid), etc., the standard enthalpy of formation ($\boldsymbol{\bar{h}^{0}_{f,i}}$) is assigned a value of zero. For other species, its formation is considered to occur by the reactions of the above-mentioned basic elements. For example, CO is considered to be formed by the reaction at standard state between C (graphite) and O_2, written as,

$$C\ (s) + 0.5\ O_2 \rightarrow CO$$

Similarly, hydrocarbon fuel species are formed by the reaction between C (graphite) and H_2. $\Delta\boldsymbol{\bar{h}_i(T)}$**,** is the enthalpy associated with the temperature change for that species. It is called sensible enthalpy. This is the increase in the enthalpy due to an increase in the temperature from the standard value (298 K) to a higher temperature, T (K).

Heat calculation for methane oxidation:

For methane oxidation in air, the first law is written as,

$$\dot{Q} = \bar{h}_{CO_2}(T_P) + 2\bar{h}_{H_2O}(T_P) + 7.52\bar{h}_{N_2}(T_P) - \bar{h}_{CH_4}(T_R) - 2\bar{h}_{O_2}(T_R) - 7.52\bar{h}_{N_2}(T_R)$$

For standard enthalpy for formation, neglecting superscript 0, the standard heat of reaction is calculated as,

$$\dot{Q} = \bar{h}_{f,CO_2}(T_{ref}) + 2\bar{h}_{f,H_2O}(T_{ref}) + 7.52\bar{h}_{f,N_2}(T_{ref}) - \bar{h}_{f,\,CH_4}(T_{ref}) - 2\bar{h}_{f,O_2}(T_{ref}) - 7.52\bar{h}_{f,N_2}(T_{ref})$$

Since, the enthalpies of formation for O2 and N2 are zero,

$$\dot{Q} = \bar{h}_{f,CO_2}(T_{ref}) + 2\bar{h}_{f,H_2O}(T_{ref}) - \bar{h}_{f,\,CH_4}(T_{ref})$$

$$\dot{Q} = -393.52 + 2(-241.83) - (-74.5) = -802.68\ kJ/mol - CH_4$$

Standard heat of reaction & heat of combustion:

It is clear that the value of standard heat of reaction is negative, since heat is released from the control volume to the surroundings (exothermic reaction).

Further, this value is obtained per mole of methane, since the reaction between methane and air is written considering one mole (or kmol) of methane. This may be converted to per kg of methane by dividing the value by molecular mass of methane. That is, standard heat of reaction per kg of methane is -802.68 × 1000 / 16 = -50167.5 kJ/kg-CH_4 or -50.2 MJ/kg-CH_4.

Standard heat of combustion or the heating value or the calorific value is just the negative of the standard heat of reaction. Thus, the heating value of methane is 50.2 MJ/kg-CH_4. This is the heat received by the surroundings, which is positive.

Higher and lower calorific values:

In the above calculation, water in the product is taken to be in vapor state (the enthalpy of formation of water vapor has been used). Thus, there is some amount of energy available in the product gas equal to latent heat of vaporization of water vapor that can be extracted. Therefore, the heating value, thus obtained, is called the lower heating value.

On the other hand, if the water in the products is considered to be in liquid state, using the enthalpy of formation of liquid water equal to -283.83 kJ/mol, the latent heat of water vapor has already been extracted. In this case, higher heating value is obtained.

In reality, some water in the products can condense on walls and surfaces and some remain in vapor state. Therefore, practically, the heat of combustion will be in between the higher and lower heating values.

Standard heat of combustion per kg of oxygen:

The heat of reaction can be calculated per mole and per kg of oxygen consumed during the combustion. For instance, the standard heat of reaction of methane is calculated per mol of oxygen, as,

$$-802.68 / 2 = -401.34 \text{ kJ/mol-}O_2,$$

since for one mole of methane burnt, 2 moles of oxygen are burnt. The heat of reaction on oxygen mass basis is:

$$-401.34 \times 1000 / 32 = -12542 \text{ kJ/kg-}O_2$$

or heat of combustion per kg of oxygen consumed is 12.54 MJ/kg-O_2.

If the same calculations are carried out for methanol, the values of heat of combustion are obtained as 19.9 MJ/kg-methanol and 13.3 MJ/kg-O_2. Thus, it can be shown that the heat of combustion per kg-oxygen, for several fire sources (fuels) lies within 13.1 ± 0.7 MJ/kg-O2. This concept is used in oxygen calorimetry.

Standard heat of combustion per kg of CO_2:

Similarly, the standard heat of combustion per kg-CO_2 produced is: 802.68 × 1000 / 44 = 18243 kJ/kg-CO_2. In fact, this is an extreme value obtained for methane combustion. For pentane to dodecane, this value lies in a smaller range, given as: 14.7 MJ/kg-CO_2 to 14.2 MJ/kg-CO_2. The average value of heat of combustion per kg-CO_2, for several fuels is 13.3 ± 1.5 MJ/kg-CO_2. This concept is used in carbon-dioxide calorimetry.

Standard heat of combustion of liquid fuel:

The stoichiometric combustion of n-heptane (C7H16), a commonly used liquid fuel, is given as,

$$C_7H_{16} + 11(O_2 + 3.76N_2) \rightarrow 7CO_2 + 8H_2O + 41.36N_2$$

Standard enthalpy of formation of gaseous (or vapor) n-heptane is -189.3 kJ/mol and that of liquid n-heptane is -225.9 kJ/mol. Based on the state of the fuel, liquid or vapor, appropriate value of enthalpy of formation is to be used.

On mass basis, the heat of reaction of vapor heptane can be calculated as -45000 kJ/kg-fuel. Here, water is in vapor state. Thus, the lower calorific value of n-heptane is 45 MJ/kg-heptane. The lower heating value of n-heptane, if it is in liquid state initially, can be shown to be 44.6 MJ/kg.

Heat of combustion:

Standard heat of combustion is obtained when reactant enter and products leave at standard conditions of 1 atm and 298 K. If the products exit the control volume at a higher temperature, the heat of combustion will be lower than the standard value.

For example, consider n-heptane burning with 125% stoichiometric air, written as,

$$C_7H_{16} + 13.75(O_2 + 3.76N_2) \rightarrow 7CO_2 + 8H_2O + 2.75O_2 + 51.7N_2$$

If the reactants enter at 298 K and the products leave at 1200 K, the heat of reaction is calculated as follows:

$$\dot{Q} = 7\left[-393.52 + \Delta\bar{h}_{CO_2}(1200)\right] + 8\left[-241.83 + \Delta\bar{h}_{H_2O}(1200)\right] +$$

$$2.75\Delta\bar{h}_{O_2}(1200) + 51.7\Delta\bar{h}_{N_2}(1200) - (-189.3)$$

Sensible enthalpy:

Sensible enthalpies are obtained from tabulated data or from specific heat data that is usually available as a piece-wise polynomial of temperature (NIST database) as shown below:

$$\Delta\bar{h}_i(1200) = \int_{298}^{1200} C_{p,i}(T)dT = 1000\int_{298}^{1200}(A + BT^* + CT^{*2} + DT^{*3} + ET^{*-2})dT^*$$

Here, T* = (T/1000). For instance, considering i = CO_2, A = 24.99735, B = 55.18696, C = -33.69137, D = 7.948387, E = -0.136638 (NIST database). Using such expressions, $\dot{Q}$ is got as:

$$\dot{Q} = 7[-393.52 + 44.47] + 8[-241.83 + 34.51] + 2.75(29.7) + 51.7(28.11) - (-189.3)$$

$$\dot{Q} = -2377.65 \text{ kJ/mol} - \mathrm{C_7H_{16}}$$

Heat calculation for multicomponent fuel:

Consider LPG that 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. Volume fractions translate to mole fractions. For example, mole fraction of propane, $X_{propane}$, in LPG is 0.1331.

Molecular weight of LPG is obtained by a chain mixing rule called Kay's rule, given as,

$$MW_{LPG} = \sum (X_i \times MW_i).$$

Here, X_i is the mole fraction of the i_{th} species and MW_i is its molecular mass. Molecular mass of LPG is obtained as 54.2 kg/kmol.

Standard enthalpy of formation of LPG is obtained using similar chain rule, given as,

$$\bar{h}^{0}_{f,LPG} = \sum\left(X_i \times \bar{h}^{o}_{f,i}\right) \ \ \mathrm{kJ/mol}$$

It should be noted that if mass fractions of the constituents of LPG have been given, then, the values of enthalpies of formation of individual species used in the calculations should be specific to mass (kJ/kg). These are obtained by dividing the molar enthalpy of formation (kJ/kmol) of a component by its molecular mass (kg/kmol). Mixture enthalpy of formation (for LPG) may be converted back to molar form by using the molecular mass of the mixture, MW_{LPG}. Global single step reaction of LPG and air, as shown earlier, is written as,

$$C_{3.77}H_{8.98} + 6.015(O_2 + 3.76N_2) \rightarrow 3.77CO_2 + 4.49H_2O + 22.6N_2$$

Standard heat of reaction of LPG and air is calculated as,

$$\dot{Q} = 3.77\bar{h}_{f,CO_2}(298) + 4.49\bar{h}_{f,H_2O}(298) - \bar{h}_{f,\,LPG}(298)$$