Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 03

Lecture – 04

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

Example calculation – no dissociation:

Here, $\overline{\mathrm{h}}_{\mathrm{f,CO_2}}(298)$ is the standard heat of formation of CO_2. $\Delta\bar{h}_i$ (i = CO_2, O_2, N_2) represents the sensible heat. Since the enthalpy of the reactant is zero, the value of T_P should be such that the value of H_P is zero. For this, a value of T_P is assumed. In the NIST database, the values of standard enthalpies of several species are listed as a polynomial of temperature. Using the polynomial, plugging the assumed value of T_P, H_P is evaluated.

If (H_P – 0) is < 10^{-5} (a very small number), then that value of T_P is the adiabatic flame temperature.

For char combustion, when T_P is assumed as 1800 K, the value of H_P is -12.011 kJ. When T_P is assumed as 1900 K, the value of H_P is 15.9 kJ. Thus, by linear interpolation, the correct value of T_P is estimated as 1843 K. This is a realistic value for the given case.

Example calculation – considering dissociation:

Consider an adiabatic flow reactor in which vaporized benzene (C_6H_6) and stoichiometric air flow steadily at 1 atm, 298 K, and the products of combustion leave the reactor.

$$C_6H_6 + 7.5(O_2 + 3.76N_2) \rightarrow 6CO_2 + 3H_2O + 28.2N_2$$

If the dissociation of CO_2 and H_2O is neglected, the adiabatic flame temperature is obtained by a similar calculation illustrated above, as 2529 K. If the dissociation of CO_2 & H_2O is considered, using the chemical equilibrium approach, the adiabatic flame temperature is evaluated as 2341 K. This calculation is done using NASA CEA. Mole fractions of CO, CO_2, H_2, and H_2O in the product mixture at the equilibrium temperature are evaluated as 0.0215, 0.1374, 0.002 and 0.075, respectively.

Simplified approach for flame temperature:

A thermodynamic approach can be used to evaluate the flame temperature using the specific heat of the product mixture, calculated at an average temperature. There are several thumb rules available in literature illustrating the value of the average temperature used to obtain properties such as specific heat.

Consider the stoichiometric reaction of benzene vapor and air:

$$C_6H_6 + 7.5(O_2 + 3.76N_2) \rightarrow 6CO_2 + 3H_2O + 28.2N_2$$

Enthalpies of reactant and product, expressing the sensible enthalpy in terms of specific heat at constant pressure of the mixture, are written as,

$$H_R = \bar{h}_{f,\,Benzene}$$

$$H_P = 6(-393.52) + 6(-241.83) + n_P \bar{c}_{p,mix}(T_P - 298)$$

Flame temperature using mixture-specific heat:

Here, n_P is the total number of product moles, equal to 37.2 as per single-step chemical reaction. Molar specific heat at constant pressure of the product mixture is evaluated using the mole fractions of individual species and Kay's rule as:

$$\bar{c}_{p,mix} = \sum \left(X_i \bar{c}_{p,i}\right) \ \mathrm{kJ/mol.K}$$

The mole fraction of CO_2 is 0.161, H_2O is 0.081 and N_2 is 0.758. Values of molar specific heats of individual species are evaluated at an average temperature (T_{avg}).

Choice of average temperature:

It can be recognized that to calculate the adiabatic flame temperature, $H_R = H_P$. Therefore, the problem of estimating T_P, simplifies to solving the following equation.

$$\mathrm{T_P} - 298 = (\mathrm{H_R} - [6(-393.52) + 3(-241.83)])/(\mathrm{n_P} \times \bar{\mathrm{c}}_{\mathrm{p,mix}})$$

$$\Rightarrow \mathrm{T_P} = 298 + \left[\frac{(82.93 - [6(-393.52) + 3(-241.83)])}{\mathrm{n_P} \times \bar{\mathrm{c}}_{\mathrm{p,mix}}}\right]$$

Let $c_{p,mix}$ be evaluated at 298 K. Values of c_p in kJ/kg-K for CO_2, H_2O and N_2, at 298 K are 0.844, 1.93 and 1.04, respectively. Mixture specific heat is calculated as,

$$\bar{\mathrm{c}}_{\mathrm{p,mix}} = (0.161 \times 0.844 \times 44 + 0.081 \times 1.93 \times 18 + 0.758 \times 1.04 \times 28)/1000 \ \mathrm{kJ/mol.K}$$

With this value, T_P is evaluated as 3058 K, which is unrealistic.

Let specific heats at constant pressure be calculated at 1200 K, which is typically an average temperature in a reactive flow field. Values of c_p in kJ/kg-K, at 1200 K, for CO_2, H_2O and N_2, are 1.28, 2.43 and 1.2, respectively.

$$\bar{\mathrm{c}}_{\mathrm{p,mix}} = 0.0381 \ \mathrm{kJ/mol.K}$$

With this value of mixture specific heat, TP is evaluated as 2534 K. This is a better estimation. The procedure can still be simplified. Since nitrogen is the primary constituent in the products of combustion using air, the specific heat of the mixture is approximated as specific heat of nitrogen. Based on the application and necessity of the accuracy of the data, a proper approach with necessary details is adopted.

Analysis of systems:

Till this point, a flow reactor (control volume) has been considered in the analysis of heat and temperature calculations. A system is considered to understand a device or closed compartment, where the mass remains constant during the analysis and volume may vary. As the first example, a piston-cylinder arrangement is considered, where combustion of a fuel with an oxidizer takes place in the volume in the cylinder, enclosed by the piston. The first law of thermodynamics for the system, in the absence of changes in potential and kinetic energies, is written as, $Q - W = E_2 - E_1 = U_2 - U_1$

Here, Q is the heat interaction, W is the displacement work originating due to movement of the piston causing a volume change and $(U_2 - U_1)$ is the change in the internal energy.

Reaction at constant pressure:

When a combustion reaction takes place inside the cylinder, the piston rises up to maintain the pressure constant at the value of the initial reactant pressure. The displacement work for a volume change of $(V_2 - V_1)$, is calculated as $p \times (V_2 - V_1)$. The first law is now written as,

$$Q - p(V_2 - V_1) = U_2 - U_1$$

$$Q = p(V_2 - V_1) + U_2 - U_1 = H_2 - H_1 = \Delta H_R.$$

Enthalpy of reactant (H_1) and product (H_2) are calculated using similar way using enthalpy of formation and sensible enthalpy. For exothermic reactions, ΔH_R is negative and heat is transferred from system to the surroundings. If the system is adiabatic, the products will reach the maximum temperature, the adiabatic flame temperature.

Reaction at constant volume:

If the system is a rigid such that its volume remains constant, similar to a closed compartment, where a fire is initiated, noting that displacement work will be zero as $\Delta V = 0$, the first law is written as,

$$Q = U_2 – U_1 = U_P – U_R$$

The heat of reaction in this case is the difference between the internal energies of the product mixture and the reactant mixture.

Internal energy is obtained using the values of enthalpy:

$$U_P = H_P - p_P \times V \text{ and } U_R = H_R – p_R \times V$$

Gas mixture inside the system is treated as an ideal gas mixture, obeying: $pV = nR_uT$. Here, n is the number of moles of the mixture and Ru is the universal gas constant. Using this,

$$U_P = H_P – n_PR_uT_P \text{ and } U_R = H_R – n_RR_uT_R$$