Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 03

Lecture – 05

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

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,

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

Constant volume combustor – pressure rise:

Let a closed rigid container contain propene, C_3H_6, and 150% theoretical air at 100 kPa and 298 K.

Let the mixture be ignited and complete combustion takes place. Let heat be transferred so that the temperature of the products is maintained at 1200 K.

The chemical reaction is written as:

$$C_3H_6 + 6.75(O_2 + 3.76N_2) \rightarrow 3CO_2 + 3H_2O + 2.25O_2 + 25.38N_2$$

Final pressure is estimated using the equation of state, noting that the volume remains constant. State 1 is that of reactant and state 2 is that of products. Number of moles of reactants and products being $n_1 = 33.13$ and $n_2 = 33.63$, respectively, the final pressure is estimated using,

$$p_2/p_1 = n_2T_2/(n_1T_1)$$

$$\Rightarrow p_2 = 100(33.63\times1200)/(33.13\times298) = 408.76\ kPa$$

Constant volume combustor – heat of reaction:

Applying first law to the system:

$Q = U_2 - U_1 = (H_2 - n_2 R_u T_2) - (H_1 - n_1 R_u T_1)$

The values of enthalpies are calculated by the usual procedure.

$$H_1 = 1 \times \bar{h}_{f,propene} = 20.41\ kJ$$

$$H_2 = 3\left(-393.52 + \Delta\bar{h}_{CO_2}(1200)\right)$$

$$+3\left(-241.83 + \Delta\bar{h}_{H_2O}(1200)\right)$$

$$+2.25\Delta\bar{h}_{O_2}(1200) + 25.38\Delta\bar{h}_{N_2}(1200)$$

Substituting the values from NIST database, H_2 = -887.84 kJ.

The heat of interaction is calculated as,

$Q = -887.84 - 33.63\times 8.31415\times 10^{-3}\times 1200 - (20.41 - 33.13\times 8.31415\times 10^{-3}\times 298)$

$\Rightarrow Q = -1161.69$ kJ/mol-C_3H_6.

Chemical kinetics - global reaction:

Chemical kinetics is used to evaluate the rate at which a reaction takes place. Rate of a reaction primarily depends upon the temperature and the concentrations of the reactants.When a reaction represents the overall reactants and major products, it is generally called a global reaction. An example:

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

A global reaction cannot occur in a single step as shown above nor it is reversible. The numbers in front of the species represent the number of moles; here, 1 kmol of CO_2, 2 kmol H_2O, etc.

Elementary reaction:

A global reaction usually occurs in several steps. These steps are part of a chain reaction having four stages. First stage, as a result of which, reactants are disintegrated (their bonds are broken), is called chain initiation. This also forms some species called radicals, which are highly reactive. Second stage is called chain propagation. Here, meta stable species and radicals are formed. Third stage is called chain branching. This stage accelerates the overall reaction by producing multiple highly reactive radicals. Final stage is called chain termination. Here, major products such as CO_2 and H_2O are formed by the reactions involving radicals. These four stages occur simultaneously. All these chain reactions are elementary reactions. They are molecular level reactions and are reversible.

Examples for elementary reactions: consider methane + oxygen as reactants. Here, M is *third body* (other species or even wall).

$O_2 \ (+M) \leftrightarrow 2O \ (+M)$ (initiation)

$O_2 + CH_4 \leftrightarrow HO_2 + CH_3$ (initiation)

$CH_4 \ (+M) \leftrightarrow CH_3 + H \ (+M)$ (initiation)

$O + H \leftrightarrow OH$ (branching)

$H + O_2 \leftrightarrow O + OH$ (branching)

$CH_3 + OH \leftrightarrow CH_3O + H$ (propagation)

$H + CH_3O \leftrightarrow H_2 + CH_2O$ (propagation)

$CH_2O \ (+M) \leftrightarrow H_2 + CO \ (+M)$ (propagation)

$H + CH_2O \leftrightarrow HCO + H_2$ (propagation)

$OH + H_2 \leftrightarrow H + H_2O$ (propagation)

$CO + OH \leftrightarrow CO_2 + H$ (propagation)

$H + OH \ (+M) \leftrightarrow H_2O \ (+M)$; $CO + O \ (+M) \leftrightarrow CO_2 \ (+M)$ (termination)