Module 7

Reactive Mixtures

Lecture 7.1

Mass and Energy Balance

THERMODYNAMICS OF REACTIVE MIXTURES

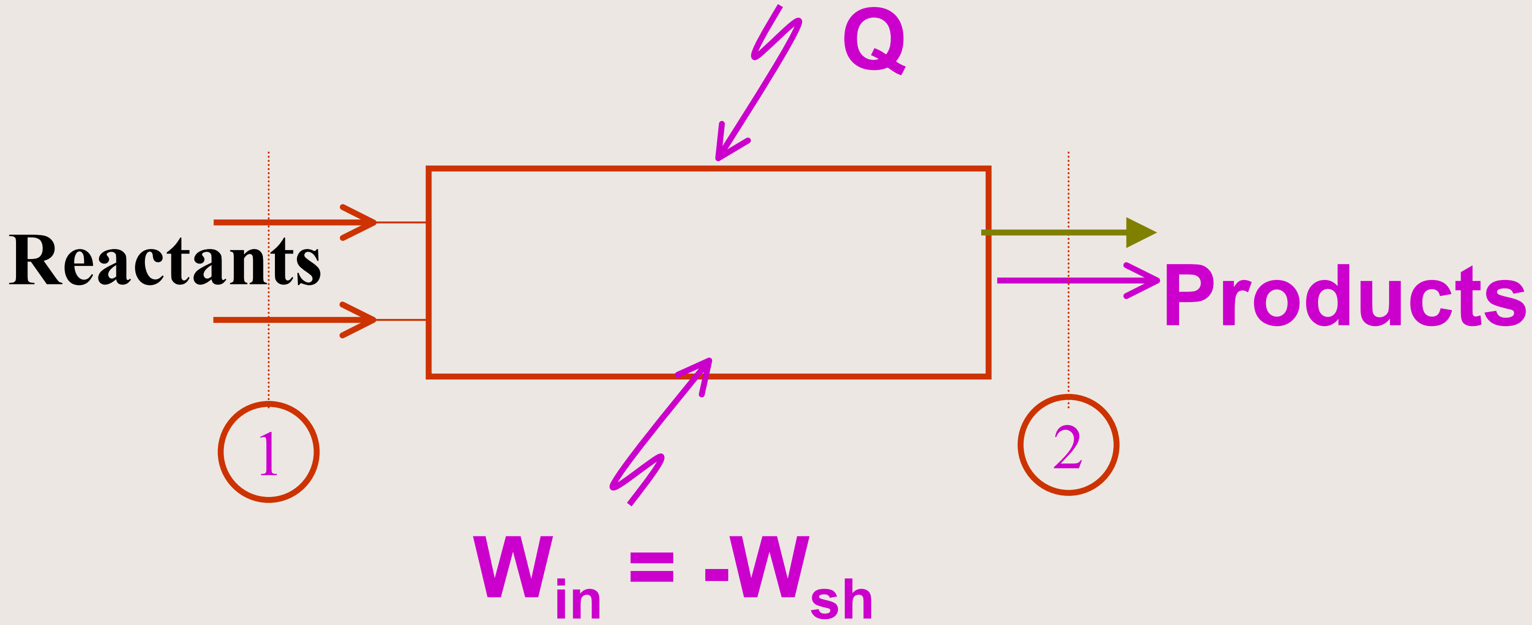
- Special feature : Inter atomic bonds in molecules of reactants are broken followed by rearrangement of atoms to form new compounds
- Thermodynamic analysis:
  - Mass balance
  - Energy Balance
  - Equilibrium Study

THERMODYNAMICS OF REACTIVE MIXTURES

- MASS BALANCE … Stoichiometry
- Cons. of mass for each species.
- Examples : Combustion of fuels
- **Octane is burnt with 95% of theoretical air; write its combustion equation**
- Stoichiometric eq: $C_8H_{18}+12.5O_2=8CO_2+9H_2O$
- **with 95 % air**
- $C_8H_{18}+12.5\times.95(O_2+3.76N_2)=?CO_2+?H_2O+?CO+?N_2$

THERMODYNAMICS OF REACTIVE MIXTURES

- First Law Analysis



THERMODYNAMICS OF REACTIVE MIXTURE

$$Q + H_{R1} = H_{P2} - W_{in} = H_{P2} + W_{SH}$$

$$Q = \sum \bar{h}_{Pi} N_{Pi} - \sum \bar{h}_{Ri} N_{Ri} + W_{SH}$$

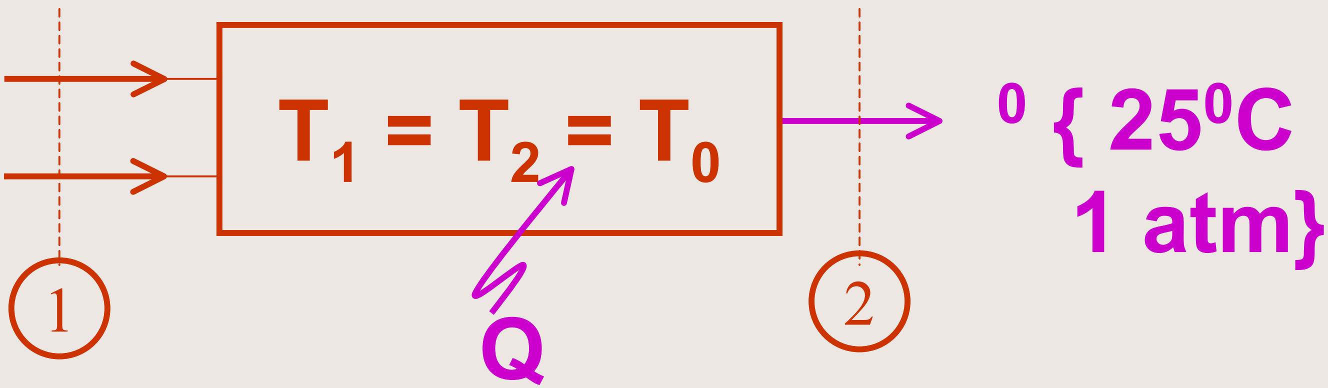
Need for absolute values or enthalpies

$$Q = \sum \left(\bar{h}_{P2} - \bar{h}_{P0}\right)_i N_{Pi} - \sum \left(\bar{h}_{R1} - \bar{h}_{R0}\right) N_{Ri}$$

$$+ \underbrace{\left(\sum h_{P0} N_{Pi} - \sum h_{R0} N_{Ri}\right)}_{\text{Enthalpy of reaction : } \triangle H^0} + W_{SH}$$

THERMODYNAMICS OF REACTIVE MIXTURE

ENTHALPY OF REACTION $\triangle H^0$



$$Q = \sum h_{P0}\ N_{Pi} - \sum h_{R0}\ N_{Ri} = \Delta H^0$$

$\triangle H > 0$ -----Endothermic

$\triangle H < 0$ -----Exothermic

THERMODYNAMICS OF REACTIVE MIXTURE

COMBUSTION OF FUELS : **Heating value of fuel**

$- \triangle H^0 =$ HHV & LHV

LHV : H_2O appears in the gas phase

HHV : H_20 appears in the liquid phase

THERMODYNAMICS OF REACTIVE MIXTURE

ENTHALPY OF FORMATION $\triangle H_F$

$\triangle H_F = \triangle H^0$ for the reaction producing the compound from its elements.

$$\Delta h_F = h_{comp} - \sum_i \left(\upsilon_i h_i\right)_{elements}$$

Molal enthalpy of the compound

Stoichiometric coeff. of i^{th} element in forming a single mole of the compound

THERMODYNAMICS OF REACTIVE MIXTURE

Convention : assign a value of zero to the enthalpy of all stable elements at 25^0C and 1 atm.

$$\therefore \triangle h_F = h_{comp.}$$

$$\therefore \Delta H^0 = \sum \left(n_i h_i\right)_P - \sum \left(n_i h_i\right)_R$$

Std. enthalpy of reaction

products

reactants

Stoichiometric coeff.

$$= \sum_P \left(n_i \left(\Delta h_F\right)_i\right) - \sum_R \left(n_i \left(\Delta h_F\right)_i\right)$$

THERMODYNAMICS OF REACTIVE MIXTURE

$\therefore$ **First law statement for S.S.S.F. chem. reaction :**

$$Q=\sum_{P} n_i\left(h_{P2}-h_{P0}\right)_i-\sum_{R} n_i\left(h_{R1}-h_{R0}\right)_i$$

$$+\sum_{P}\left(n_i\Delta h_F\right)_i-\sum_{R} n_i\left(\Delta h_F\right)_i+W_{SH}$$

$$Q=\sum_{P} n_i\overline{h}_i-\sum_{R} n_i\overline{h}_i+W_{SH}$$

where $\overline{h}_i=\left(h_{T,P}-h_{298K,1atm}\right)_i+\left(\Delta h_F\right)_i$

Example

- **Steady flow combustion of Propane at 25C with 100% excess air . Products leave at 500K find the heat transfer.**
- $C_3H_8 + 10(O_2 + 3.76N_2) = 3CO_2 + 4H_2O + 5O_2 + 37.6N_2$
- **applying the SSSF equation**

$$Q = \sum_P n_i \bar{h}_i - \sum_R n_i \bar{h}_i + W_{SH}$$

where $$\bar{h}_i = \left(h_{T,P} - h_{298K,1atm}\right)_i + \left(\Delta h_F\right)_i$$

Substituting values from tables get : Q= -1.738 $\times 10^6$ kJ

THERMODYNAMICS OF REACTIVE MIXTURE

ADIABATIC FLAME TEMP.

SSSF process with Q = 0; $W_{SH} = 0$

First law eq. => $\sum \left(N_i \bar{h}_i\right)_R = \sum \left(N_i \bar{h}_i\right)_P$

$$\underbrace{\sum N_i \left(h_{i(T_R)} - h_i^0 + \Delta h_{F_i}^0\right)}_{\text{Known from given reactant states}} = \underbrace{\sum_P N_i \left(h_{i(T)} - h_i^0 + \Delta h_{F_i}^0\right)}_{\text{Determine T such that its value equals LHS}}$$

Known from given reactant states

Determine T such that its value equals LHS

End of Lecture