Module 7

Reactive Mixtures
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: \( \text{C}_8\text{H}_{18} + 12.5\text{O}_2 = 8\text{CO}_2 + 9\text{H}_2\text{O} \)
• with 95% air
• \( \text{C}_8\text{H}_{18} + 12.5 \times 0.95(\text{O}_2 + 3.76\text{N}_2) = ?\text{CO}_2 + ?\text{H}_2\text{O} + ?\text{CO} + ?\text{N}_2 \)
THERMODYNAMICS OF REACTIVE MIXTURES

• First Law Analysis

\[ W_{in} = -W_{sh} \]
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

\[ Q = \sum \left( \bar{h}_{P2} - \bar{h}_{P0} \right)_i N_{Pi} - \sum \left( \bar{h}_{R1} - \bar{h}_{R0} \right) N_{Ri} + \left( \sum h_{P0} N_{Pi} - \sum h_{R0} N_{Ri} \right) + W_{SH} \]

Enthalpy of reaction: \( \Delta H^0 \)
THERMODYNAMICS OF REACTIVE MIXTURE

ENTHALPY OF REACTION

\[ \Delta H^0 \]

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

\( \Delta H > 0 \) ----- Endothermic

\( \Delta H < 0 \) ----- Exothermic
THERMODYNAMICS OF REACTIVE MIXTURE

COMBUSTION OF FUELS: Heating value of fuel

- $\Delta H^0 = \text{HHV} & \text{LHV}$

LHV: $\text{H}_2\text{O}$ appears in the gas phase

HHV: $\text{H}_2\text{O}$ appears in the liquid phase
ENTHALPY OF FORMATION $\Delta H_F$

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

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

Molal enthalpy of the compound

Stoichiometric coeff. of $i^{th}$ element in forming a single mole of the compound
Convention: assign a value of zero to the enthalpy of all stable elements at 25°C and 1 atm.

\[ \Delta h_F = h_{\text{comp}}. \]

\[ \Delta H^0 = \sum (n_i h_i)_P - \sum (n_i h_i)_R \]

Std. enthalpy of reaction

Stoichiometric coeff.

\[ = \sum_{P} (n_i (\Delta h_F)_i) - \sum_{R} (n_i (\Delta h_F)_i) \]
THERMODYNAMICS OF REACTIVE MIXTURE

First law statement for S.S.S.F. chem. reaction:

\[
Q = \sum_P n_i (h_{P2} - h_{P0})_i - \sum_R n_i (h_{R1} - h_{R0})_i \\
+ \sum_P (n_i \Delta h_F)_i - \sum_R n_i (\Delta h_F)_i + W_{SH}
\]

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

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

- Steady flow combustion of Propane at 25°C with 100% excess air. Products leave at 500K. Find the heat transfer.

- \( \text{C}_3\text{H}_8 + 10(\text{O}_2 + 3.76\text{N}_2) = 3\text{CO}_2 + 4\text{H}_2\text{O} + 5\text{O}_2 + 37.6\text{N}_2 \)

- 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: \( Q = -1.738 \times 10^6 \text{ kJ} \)
ADIABATIC FLAME TEMP.

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

First law eq. $\Rightarrow \sum (N_i \overline{h}_i)_R = \sum (N_i \overline{h}_i)_P$

$$\sum N_i \left( h_{i(T_R)} - h_i^0 + \Delta h_{F_i}^0 \right) = \sum P N_i \left( h_{i(T)} - h_i^0 + \Delta h_{F_i}^0 \right)$$

Known from given reactant states

Determine $T$ such that its value equals LHS
End of Lecture