ME 354 Lecture Summary

Week 12: Lecture 1

Conservation of Energy for Reacting Systems

Enthalpy of Formation

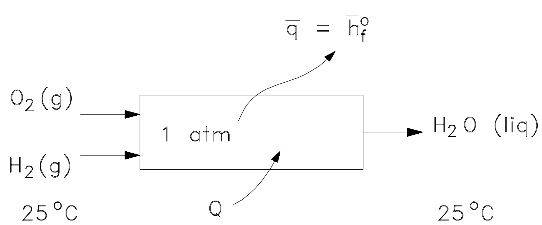
- previous calculations involving enthalpy were all based on differences and the reference used to determine enthalpy did not matter
- when chemical reactions occur, reactants disappear and products are formed $\rightarrow$ differences cannot be calculated for all substances involved
- it is necessary to establish a common base to account for differences in composition
- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure
  - $T_{ref} = 25°C \rightarrow 298\ K$
  - $P_{ref} = 1\ atm$
- $h = 0$ assigned to elements in their most stable form i.e. $O_2, N_2, C, etc.$
- the enthalpy of formation is defined as:
  - the energy released or absorbed when a compound is formed from its stable elements at STP

$$\delta\overline{h}_f^o = \overline{h}_{comp}^o - \sum \overline{n_i}\overline{h}_i^o \quad (kJ/kmole)$$

where

$\overline{n}_i$ = # of moles of i'th elemental substance in forming a single mole of compound (unitless)

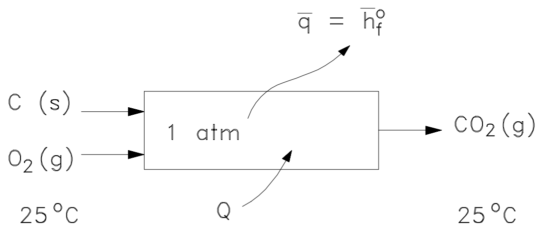
Consider the following reactions taking place at atmospheric pressure, such that $T_{prod} = T_{react} = 298\ K$



$$\frac{1}{2}O_2 + H_2 \rightarrow H_2O$$

where $\overline{h}_f^o = -286\ MJ/kmole\ of\, H_2O$ (heat transferred from the combustion chamber)

Week 12: Lecture 1



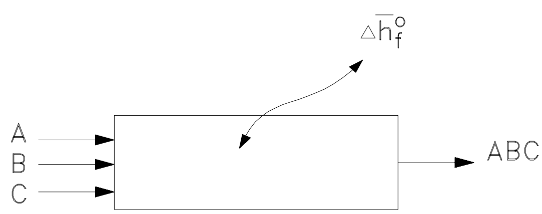
$$C + O_2 \rightarrow CO_2$$

where $\overline{h}_f^o = -393\ MJ/kmole\ of CO_2$ (heat transferred from the combustion chamber)

These reactions are called formation reactions because a substance is formed from its elements in their respective natural states at STP

$$\overline{q} = standard\ heats\ of\ formation$$

$$\overline{h}_f^o = enthalpy\ of\ formation$$



$$\delta \overline{h}_f^o = \overline{h}_{comp}^o - \sum \overline{n}_i \overline{h}_i^o \quad (kJ/kmole)$$

An energy balance gives

$$\underbrace{a\overline{h}_A^o + b\overline{h}_B^o + c\overline{h}_C^o}_{generally\ 0} + \delta \overline{h}_f^o \rightarrow \overline{h}_{ABC}^o$$

If

$\overline{h}_f^o > 0$ - endothermic

$\overline{h}_f^o < 0$ - exothermic

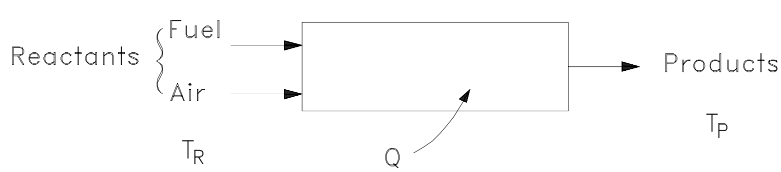
Week 12: Lecture 2

Enthalpy of Combustion

- for various types of fuels the enthalpy of formation is not always known
  - the chemical composition of most fuels may vary from batch to batch
  - generally not tabulated
- enthalpy of combustion is an experimental alternative to enthalpy of formation
  - defined as the difference between the enthalpy of the products and the enthalpy of the reactants where complete combustion occurs at a given temperature and pressure

$$Q = \sum (mh)_P - \sum (mh)_R = H_P(T_P) - H_R(T_R)$$

$$Q = \sum (n\overline{h})_P - \sum (n\overline{h})_R = \underbrace{\overline{H}_P(T_P) - \overline{H}_R(T_R)}_{H_{RP}}$$



- when enthalpy of formation data is available for all products and reactants the above equation can be used
- otherwise a calorimeter must be used to measure the enthalpy of combustion
- $+ve\ Q \Rightarrow$ endothermic reaction
- $-ve\ Q \Rightarrow$ exothermic reaction

Heating Value

- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion

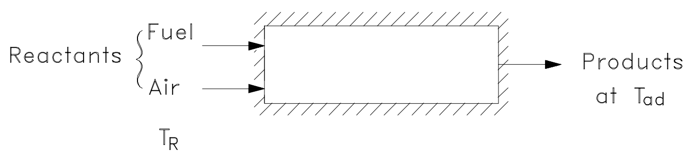
Week 12: Lecture 2

- two values are used
  - HHV: higher heating value - obtained when all the water formed by combustion is a liquid
  - LHV: lower heating value - obtained when all the water formed by combustion is a vapour
- the HHV exceeds the LHV by the energy required to vaporize the liquid formed

$$HHV = LHV + (mh_{fg})_{H_2O}$$

Adiabatic Flame Temperature

- under adiabatic conditions the maximum temperature attained by the products when combustion is complete is called the adiabatic flame or adiabatic combustion temperature



$$H_P(T_{ad}) = H_R(T_R)$$

$$\sum_P n_e(\overline{h}_f^o + \Delta\overline{h})_e = \sum_R n_i(\overline{h}_f^o + \Delta\overline{h})_i$$

$$\sum_P n_e(\Delta\overline{h})_e = \sum_R n_i(\Delta\overline{h})_i + \sum_R n_i\overline{h}_{f_i}^o - \sum_P n_e\overline{h}_{f_e}^o$$

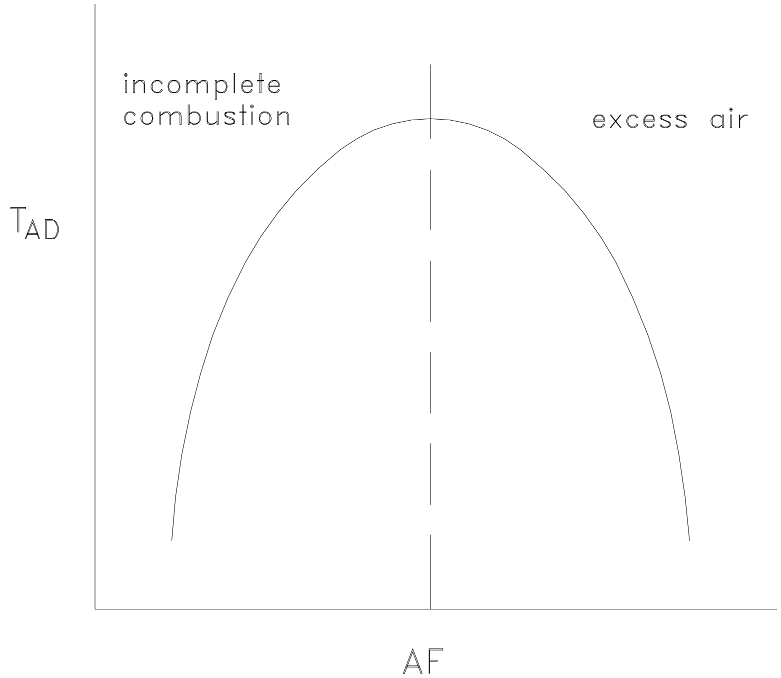
where

n	-	obtained from reaction equation
$\overline{h}_{f_i}^o$	-	from tabulated data
$\Delta\overline{h}$	-	from tables or calculated knowing T_R

Therefore all terms on the right hand side can be evaluated. While the left hand side accounts for the change in enthalpy from T_{ref} to T_{ad}, which is unknown. The procedure requires iteration.

The temperature for the products is assumed. We then keep trying until we get agreement with the RHS. A typical value of $T_{ad} \approx 2300\ K$ for most hydro carbon fuels

Week 12: Lecture 2



Week 12: Lecture 3

Evaluation of Entropy for Reacting Systems

- a common datum must be used to assign entropy values for each substance involved in the reaction
- an entropy of 0 for pure crystalline substances is obtained at absolute zero
- the entropy relative to this datum is called absolute entropy
- absolute entropy at 1 atm and temperature T is denoted as $s^o(T)$ or $\overline{s}^o(T)$ for a per unit mass or per mole basis (note: referred to as $\hat{\phi}$ in Reynolds and Perkins)
- the entropy at any value of T and P can be calculated as

$$\overline{s}(T,P) = \overline{s}^o(T) - \mathcal{R}\ln\left(\frac{P_i}{P_{ref}}\right)$$

- the entropy of the i'th component of an ideal gas mixture is evaluated at temperature T and the partial pressure P_i where the partial pressure is given by

$$P_i = X_i P$$

and

$$\overline{s}(T,P_i) = \overline{s}_i^o(T) - \mathcal{R}\ln\left(\frac{X_i P}{P_{ref}}\right)$$

Incomplete Combustion

- when the amount of air supplied is less than the theoretical air required the combustion is incomplete
- the usual result is carbon unites with oxygen to form carbon monoxide (CO) instead of CO_2

Week 12: Lecture 3

Dew Point

- since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapour in the form of gaseous products can be significant
- if the gaseous products of combustion are cooled at constant mixture pressure the dew point temperature is reached when water vapour begins to condense
- since corrosion of duct work, mufflers etc. can occur, the knowledge of dew point temperature is important