Stoichiometry, Energy Balances, Heat Transfer, Chemical Equilibrium, and Adiabatic Flame Temperatures

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Stoichiometry
STOICHIOMETRY

- Outline
  - combustion reactions
  - combustion with air
  - equivalence ratio, stoichiometric ratio
  - percent theoretical air, percent excess air
  - percent excess oxygen in stack gases
  - dry and wet basis for concentrations
  - actual and theoretical concentrations
  - the effects of mixing and in leakage

\[ \text{Combustion reactions} \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]

\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \]

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]

In general

\[ nC + nO_2 \rightarrow nCO_2 \]

\[ mH + \frac{m}{4}O_2 \rightarrow \frac{m}{2}H_2O \]

or

\[ C_nH_m + \left( n + \frac{m}{4} \right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O \]
STOICHIOMETRY

- Combustion with air

Assume air is 21% O₂ and 79% N₂, by volume. Then each mole O₂ brings with it 3.76 mole N₂.

\[
C_nH_m + \left( n + \frac{m}{4} \right)O_2 + 3.76 \left( n + \frac{m}{4} \right)N_2 \rightarrow 
\]
\[
nCO_2 + \frac{m}{2}H_2O + 3.76 \left( n + \frac{m}{4} \right)N_2 
\]

STOICHIOMETRY

- Equivalence ratio

\[
\Phi = \frac{\left[ \frac{\text{mols fuel}}{\text{mols oxidant}} \right]_{\text{supplied by operator}}}{\left[ \frac{\text{mols fuel}}{\text{mols oxidant}} \right]_{\text{reqd for complete combustion}}}
\]

- Stoichiometric ratio

\[
SR = \frac{1}{\Phi}
\]

SR = 1/\Phi = 1 means that conditions are stoichiometric or chemically balanced.
STOICHIOMETRY

• \( \Phi \) and SR
  - Fuel rich (reducing): \( SR < 1 \) and \( \Phi > 1 \)
  - Fuel lean (oxidizing): \( SR > 1 \) and \( \Phi < 1 \)
  - Alternate forms w/ constant amount of fuel
    \[
    \Phi = \frac{\text{mols oxidant reqd}}{\text{mols oxidant fed}}
    \]
    \[
    SR = \frac{\text{mols oxidant fed}}{\text{mols oxidant reqd}}
    \]

STOICHIOMETRY

• Percent theoretical air
  \[
  \%TA = 100(SR) = \frac{100}{\Phi}
  \]

• Percent excess air
  \[
  \%EA = \%TA - 100 = 100(SR - 1) = 100 \left[ \frac{1}{\Phi} - 1 \right]
  \]
STOICHIOMETRY

- Percent excess oxygen in stack gases
  - Defined as actual mole (volume) percent in stack. Not to be confused with %EA or %TA.
  - Can be measured on a dry or wet basis.
- Dry or wet basis for stack measurement
  - Dry basis gives higher value because water vapor acts as a diluent and is 10 – 15% of stack gases

![Graph showing actual and theoretical concentrations](image)

STOICHIOMETRY

- Actual and theoretical concentrations

  - Effects of imperfect mixing
  - Effects of air leakage
STOICHIOMETRY

- Controlling excess air

The rise in CO is steep as you approach SR = 1 and it is insensitive to air leakage. Air flow control by CO should lead to a close approach to SR = 1.

STOICHIOMETRY

- Spreadsheets for furnace material balance calculations
  - FURN_MB.xls:balance for liquid and solid fuels
  - GAS_MB.xls:balance for gaseous fuels

- Author: Jost Wendt
ENERGY BALANCES

• Outline
  – Conservation of mass and energy
  – Example: drying salt with hot flue gas
  – Energy balances on systems that involve reactions - the absolute enthalpy
  – Example: adiabatic combustion of H₂ in air
  – Heats of combustion and higher and lower heating values
  – Energy balance on a furnace – available heat and the efficiency of combustion
ENERGY BALANCES

• Energy and mass are conserved

\[
\dot{Q} = Q_{\text{in}} + Q_{\text{out}} + \dot{W} + \sum \dot{m} (h + \frac{V^2}{2} + gz)
\]

\[
\frac{dm_{\text{CV}}}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}}
\]

ENERGY BALANCES

• Changes in kinetic and potential energy are usually small compared to changes in internal energy

Unsteady

\[
\frac{dU_{\text{CV}}}{dt} = Q_{\text{in,net}} + W_{\text{in,net}} + \dot{m}_1 h_1 - \dot{m}_2 h_2
\]

Steady

\[
Q_{\text{in,net}} + W_{\text{in,net}} + \dot{m}_1 h_1 - \dot{m}_2 h_2 = 0
\]
ENERGY BALANCES

• Drying salt with combustion gases

Flue gas at 1000°F to be used to dry 40 tons/h salt that is 3 wt. % water. The inlet temperature of the salt is 40°F. The dry salt exits the dryer at 190-210°F. What flow rate of flue gas do we need if we assume the flue gas leaves the dryer at 400°F?

\[ \dot{m}_1 = \dot{m}_4 \]
\[ \dot{m}_2 = \dot{m}_5 \]
\[ \dot{m}_3 = \dot{m}_6 \]
ENERGY BALANCES

- Drying salt with combustion gases
  – energy balance over adiabatic dryer

\[ \dot{m}_1 (h_1 - h_4) + \dot{m}_2 (h_2 - h_5) + \dot{m}_3 (h_3 - h_6) = 0 \]

\[ \dot{m}_1 = \frac{\dot{m}_2 (h_5 - h_2) + \dot{m}_3 (h_6 - h_3)}{h_1 - h_4} \]

\[ h_{fg} = 978 \text{ Btu/lb} \quad c_{pgas} = 0.254 \text{ Btu/lb}^2\text{F} \]

\[ c_{salt} = 0.21 \text{ Btu/lb}^2\text{F} \quad c_{pH2O(g)} = 0.47 \text{ Btu/lb}^2\text{F} \]

\[ c_{H2O} = 1.0 \text{ Btu/lb}^2\text{F} \]

\[ \dot{m}_1 = 36,500 \text{ lb/h} \]
ENERGY BALANCES

• Energy balances on reacting systems – the absolute enthalpy

The reference state for systems in which reactions are occurring is conveniently chosen to be the elements at $T_{ref} = 25 \, ^\circ\text{C} (298.15 \, \text{K})$ and 1 bar.

$$h_i(T) = h_{f,i}^0(T_{ref}) + \int_{T_{ref}}^{T} c_{p,i}dT$$

Absolute enthalpy

Enthalpy of formation

Sensible enthalpy at 1 bar, 298 K change

• Heat capacity as a function of $T$ (K)

$$h_i(T) = h_{f,i}^0(T_{ref}) + \int_{T_{ref}}^{T} c_{p,i}dT$$

$$\frac{c_p}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{h}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

where $T$ is in Kelvin and $R$ is the universal gas constant, $R = 8.3145 \, \text{kJ/(kmol K)}$.

Spreadsheet: ther_coef.xls
ENERGY BALANCES

• Adiabatic combustion of H₂ with air, no dissociation. What is exit temperature?

Inlet (i)
- 0.42 kmol/s H₂
- 0.21 kmol/s O₂
- 0.79 kmol/s N₂
- 300 K, 1 bar

Exit (e)
- 0.42 kmol/s H₂O
- 0.79 kmol/s N₂
- T = ?, 1 bar

\( \dot{Q}_{in} = 0 \) \hspace{1cm} \( \dot{W}_{in} = 0 \)

\[ \dot{Q}_{in,net} + \dot{W}_{in,net} + \sum_{i} \dot{n}_i h_i - \sum_{e} \dot{n}_e h_e = 0 \]

Spreadsheet: h2_flame.xls

- We have one equation in one unknown, T. This is conveniently solved in Excel with the Goal Seek tool to give an exit temperature of 2530K. If we allow for dissociation of the water (at equilibrium), \( T_e = 2390K \).

Spreadsheet: h2_flame.xls
ENERGY BALANCES

• Heats (enthalpies) of combustion and higher (gross) and lower (net) heating values (HHV and LHV)

\[ \Delta h_{rxn}^{298} = \sum_{prod} [v_p h_{fp}] - \sum_{react} [v_r h_{fr}] \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( h_f^{298} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_4 )</td>
<td>-74.600</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>0</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>-393.510</td>
</tr>
<tr>
<td>( H_2O(l) )</td>
<td>-285.830</td>
</tr>
<tr>
<td>( H_2O(g) )</td>
<td>-241.826</td>
</tr>
</tbody>
</table>

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(liq) \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(gas) \]

ENERGY BALANCES

• Heats of reaction and HHV and LHV

\[ \Delta h_{rxn}(l) = -393.51 + 2(-285.83) - \left[ (-74.6) + 0 \right] = -890.57\text{ kJ/mol CH}_4 \]

**Gross heating value**

\[ HHV = -\Delta h_{rxn}^{298}(l) = 890.57\text{ kJ/mol CH}_4 \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(liq) \]

**Net heating value**

\[ \Delta h_{rxn}(g) = -393.51 + 2(-241.826) - \left[ (-74.6) + 0 \right] = -802.56\text{ kJ/mol CH}_4 \]

\[ LHV = -\Delta h_{rxn}^{298}(g) = 802.56\text{ kJ/mol CH}_4 \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(gas) \]
ENERGY BALANCES

• Energy balance over a furnace

\[
\dot{Q}_{in,\text{net}} + \sum_{i} \dot{n}_i h_i - \sum_{e} \dot{n}_e h_e = 0
\]

\[
h_i(T) = h^o_{f,i}(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T} c_{p,i} dT
\]

\[T_{\text{ref}} = 298.15 \text{ K}\]

Use absolute enthalpies for energy balances involving reactions.

ENERGY BALANCES

• Energy balance over a furnace – available heat

\[
\dot{Q}_{\text{avail}} = \sum_{i} \dot{n}_i \left( h^o_{f,i}(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T} c_{p,i} dT \right) - \sum_{e} \dot{n}_e \left( h^o_{f,e}(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T} c_{p,e} dT \right)
\]

Available heat = gross heat input
  – latent heat loss
  – unburned fuel loss
  – sensible flue gas heat loss

Available heat = net heat input
  – unburned fuel loss
  – sensible flue gas heat loss
ENERGY BALANCES

• Thermal efficiency of a combustion process
  – Definition in terms of HHV
    \[ \eta_{\text{gross}} = \frac{\dot{Q}_{\text{avail}}}{\dot{m}_{\text{fuel}}(\text{HHV})} \]
  – Definition in terms of LLV
    \[ \eta_{\text{net}} = \frac{\dot{Q}_{\text{avail}}}{\dot{m}_{\text{fuel}}(\text{LHV})} \]