Chemical TD: Motivation

- **Previous TD Analysis**
  - considered systems where composition of fluid was “frozen” – fixed chemical composition

- **Chemically Reacting Flow**
  - but there are numerous situations in propulsion systems where chemical reactions can occur
    - burning (jet engine combustors, augmentors, rocket combustion chambers, piston engines)
    - supersonic compression (supersonic inlets)
    - supersonic expansion (rocket nozzles)
    - other (fuel cells, monopropellant decomposition)

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Basic Problem

- Usually **Given**:
  - reactant state (composition, temp., pressure)
  - constraints (heat transfer, residence time,…)

- Want to **Find**: product state \((\chi_2, T_2, p_2)\)

- **Approach**: (Equilibrium) TD analysis: conservation eqns., state eqns. (and enough time to reach equil.)

- **Issues**: how to deal with
  1. “chemical energy”
  2. specifying equilibrium composition
Approach Outline

1. Apply mass conservation
   → atom balances or balancing stoichiometric reactions

2. Apply energy conservation
   → defining chemical “energy” or enthalpy of formation

3. Apply entropy conservation (2nd Law)
   → maximize entropy to find equilibrium

Atom Balances/Stoichiometric Reactions

- If composition can change, we will see the amount of some species decrease and others increase
- Are there any constraints on this process?
  - YES – can’t change the identity of the nuclei (in absence of nuclear reactions)
    - for example, N cannot become O
- Two ways to express this
  - “balancing” stoichiometric reaction
  - atom balances

\[ 2H_2 + O_2 \leftrightarrow 2H_2O \]

\[ \text{LHS} \quad \text{RHS} \]
\[ 2n_{H_2} = 2n_{H_2O} \]
\[ 2n_{O_2} = n_{H_2O} \]
Chemical Energy

• In nonreacting TD
  – we combined all different types of energy into stagnation enthalpy,
    \[ h_o = h + u^2 / 2 \]
  – but of course, the value of \( h \) depends on our choice of reference state; does \( h(0K)=0 \) or \( h(298K)=0 \)?

• Our goal – for chemically reacting system want to find way to add chemical energy
  \[ h'_o = h + u^2 / 2 + e_{chem} \]
  – but to do so, we need to define a reference “state” where chemical energy is zero

Chemical Energy Example

• Consider the energies of \( O_2 \) and O

\[ O_2 \leftrightarrow 2O \]

• Is energy of O more or less than for \( O_2 \)?

• Which has zero chemical energy?

• Difference in energy between species is function of temp.
Chemical Energy Example

- What happens if we have multiple types of nuclei?
  - ways to define zero chemical energy state
- Example: H and O containing species at fixed temperature

\[ E_{chem} \quad \text{H}_2\text{O} \quad E_{chem} \]

Heat of “Reaction”

- What is the energy difference between the products and reactants if \( p, T \) don’t change, e.g., \( \text{H}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{O} \)

\[ Q_R \text{ or } \Delta H_R = E_{chem, \text{H}_2\text{O}} - \left( E_{chem, \text{H}_2} + \frac{1}{2} E_{chem, \text{O}_2} \right) = H_p - H_r \]

result can’t depend on what we call zero energy (reference state)

\[ \Delta H_R < 0, \text{ exothermic} \]
\[ \Delta H_R > 0, \text{ endothermic} \]

Heat of reaction is how much heat we would have to add to keep \( T \) constant (at fixed \( p \)) for specified composition change (reaction)
Heat of Formation

• Heat of reaction if form ONE mole of species $i$ from the ZERO energy species (the \textit{elements}) at fixed temperature $T$ and standard pressure ($^\circ$)

\[ \Delta h_{f,T,i}^o \]

– or on a per mass basis

\[ \Delta h_{f,T,i}^\circ \]

• Two common choices for elements
  – the (neutral) atoms
  – the most common form of a single type of nuclei at standard $T$ and $p$

NASA Tables

\textbf{JANNAF}

$\text{H}_2$, $\text{O}_2$, $\text{N}_2$, $\text{Ar}$, $\text{C}(s)_{\text{graphite}}$

Heat of Formation Example

• Consider again $\text{O}_2$ and O

\[ \frac{1}{2} \text{O}_2 \leftrightarrow O \]

• What is enthalpy of formation of $\text{O}_2$ (JANNAF)?

\[ \Delta h_{f,T,o}^o = h_o(T) - \frac{1}{2} h_{O_2}(T) \]
Heat of Formation Example

- Consider again $\text{O}_2$ and $\text{O}$

\[
\Delta H = \frac{1}{2} \bar{h}(1000\,\text{K}) - \frac{1}{2} \bar{h}(298\,\text{K})
\]

- What is the enthalpy change going from \(\frac{1}{2}\) mole of $\text{O}_2$ at 298K to $\text{O}$ at 1000K?

\[
\Delta H = \frac{1}{2} \bar{h}(1000\,\text{K}) - \frac{1}{2} \bar{h}(298\,\text{K})
\]

General Expression for Enthalpy

- So from the previous path example, we can write in general

\[
\bar{h}(T) = \left( \bar{h}(T) - \bar{h}_{\text{ref}} \right) + \Delta \bar{h}_i^\circ + \int_{\text{ref}}^{T} \bar{c}_p \, dT + \Delta \bar{h}_i^\circ
\]

or on a per mass basis

\[
h_i(T) = \left( h_i(T) - h_{\text{ref}} \right) + \Delta h_i^\circ = \int_{\text{ref}}^{T} \bar{c}_p \, dT + \Delta h_i^\circ
\]
### Example Enthalpies of Formation

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta h^o_{\text{f}, 298.15 \text{ kJ/mol}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-110.53</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-393.52</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-74.87</td>
</tr>
<tr>
<td>H</td>
<td>218.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-241.83</td>
</tr>
<tr>
<td>O</td>
<td>249.17</td>
</tr>
<tr>
<td>OH</td>
<td>38.99</td>
</tr>
</tbody>
</table>

From NIST-JANNAF database 4th edition (1998) (e.g., kinetics.nist.gov/janaf)

`can find newer updates to data`

- High formation enthalpy species
  - H, O
- Low formation enthalpy
  - CO$_2$, H$_2$O

**High energy**$\Rightarrow$ **hard to make (unstable atoms)**

**Low energy ($<<0$)**$\Rightarrow$ **very stable at “low” T**

### Composition Influence on Temperature

- So if the products have more H, O, H$_2$, O$_2$ vs. H$_2$O
  - $T_{\text{prod}}$ will be lower than if we could shift them toward water

- $\Delta h^o_{\text{f}}$
Example: Methane/Oxygen Combustor

- **Given:**
  - Gaseous methane and oxygen entering non-adiabatic combustor at 298 K, 1 bar (stagnation conditions)
  - Mass flowrate ratio of oxygen is 5\( \times \) that for methane
  - Heat loss results in 1000 K product temperature
- **Find:**
  - Heat loss rate per unit mass flow rate, \( \dot{Q}_{loss}/\dot{m} \)
- **Assume:**
  - Steady state, no "shaft" work, \( \dot{t}_{pg} \) (but not \( c_{pg} \))

\[
\begin{align*}
\text{Reactants} & : m_{O_2} \quad 298K, 1 \text{ bar} \\
\text{Products} & : m_{prod} \quad Y_i
\end{align*}
\]

\[
\begin{align*}
\text{Molar properties:} & \quad \text{MW}_{O_2} = 32, \quad \text{MW}_{CH_4} = 16 \\
\text{Assume molar properties, so use} & \quad h = h_c/\text{MW}
\end{align*}
\]

Example: Methane/Oxygen Combustor

- **Solution**
  - Mass
    \[
    \dot{m}_0 = \dot{m}_{ref} = \dot{m}
    \]
  - Energy cons. (PICO)
    \[
    \dot{m}_{CH_4} \quad 298K, 1 \text{ bar} \\
    \dot{m}_{O_2} \quad 298K, 1 \text{ bar}
    \]
    \[
    \begin{align*}
    \dot{m}_{O_2} = 5 \Rightarrow n_{O_2} & = 2.5 \\
    \dot{m}_{CH_4} & = 1 \Rightarrow n_{CH_4} = 1
    \end{align*}
    \]

- need to know composition of reactants and products
Example: Methane/Oxygen Combustor

- Solution

\[ CH_4 + 2.5O_2 \rightarrow 2H_2O + CO_2 + ?? \]

\[ \chi_{CH_4} = 1/3.5 \]
\[ \chi_{O_2} = 2/3.5 \]

\[ \Delta H_{298K} \text{ values:} \]

-CH₄: 38.179
-O₂: 22.703
-H₂O: 26.000
-CO₂: 33.397

\[ \text{Q}_{\text{loss}} / \dot{m} = 7.35 \text{ MJ/kg} \]
\[ \text{or} \]
\[ \text{MW}\text{ kg/s} \]

For just 10 kg/s, would need to have 74 MW of cooling

\[ \dot{m}_{CH_4} \] or \[ \dot{m}_{O_2} \]

\[ \dot{m}_{\text{prod}} \]

\[ \text{Y}_i \]

\[ \text{1000K, 5 bar} \]

\[ \text{AE4451} \]
Example: Methane/Oxygen Combustor

- Alternate solution

\[
\dot{Q}_{\text{loss}} / \dot{m} = ?
\]

- Mass conservation

\[
\dot{m}_{\text{air}} + \dot{m}_{\text{fuel}} = \dot{m}_{\text{prod}}
\]

- Energy conservation

\[
\dot{m}_{\text{air}} h_{\text{v3}} + \dot{m}_{\text{fuel}} h_{\text{fuel}} = \dot{m}_{\text{prod}} h_{\text{v4}}
\]

- Group chemical vs. sensible terms

\[
\left( m_a \Delta h_a + m_{\text{fuel}} \Delta h_{\text{fuel}} - m_{\text{prod}} \Delta h_{\text{prod}} \right) \equiv m_{\text{fuel}} \Delta h_R
\]

\[
\text{fuel heating value}
\]

\[
\text{energy release per mass fuel at } T_{\text{ref}}
\]

\[
~44 \text{MJ/kg for jet fuel}
\]

Simplified Eqn for Aircraft Combustor

- Want simplified expression we can use for engine cycle modeling.

- Consider an adiabatic combustor

\[
\dot{Q}_{\text{loss}} / \dot{m} = 7.36 \frac{MJ}{kg}
\]

< 1% difference from janaf.nist.gov

Product | \( \epsilon_i \) (J/molK) | S config
--- | --- | ---
298 K | 1000 K | \( \epsilon_{\text{avg}} \)
H\text{\textsubscript{2}}O | 33.590 | 41.268 | 37.43
CO\text{\textsubscript{2}} | 37.129 | 54.308 | 45.72
O\text{\textsubscript{2}} | 29.376 | 34.870 | 32.13
Simplified Eqn for Aircraft Combustor

- So
\[ m_{\text{fuel}} \Delta h_R = m_{\text{prod}} \Delta h_{\text{prod}} T_3 - m_a \Delta h_{\text{air}} T_{\text{ref}} - m_{\text{fuel}} \Delta h_{\text{fuel}} T_{\text{ref}} \]

- If we assume \( h_{\text{sens},i}(T_{\text{ref}}) = 0 \), \( T_{\text{fuel}} \approx T_{\text{ref}} \)

Fuel-Air Ratio
\[ f = \frac{m_{\text{fuel}}}{m_a} \quad f \Delta h_R = (1 + f) h_{o4} - h_{a3} \]
- assume \( c_p \), products and air have same \( c_p \), \( T_{\text{ref}} \approx 0 \)

\[ \frac{f \Delta h_R}{c_p} = (1 + f) T_{o4} - T_{o3} \]

\[ T_{o4} = \frac{T_{o3} + f \Delta h_R / c_p}{1 + f} \]

and
\[ f = \frac{T_{o4} - T_{o3}}{\Delta h_R / c_p - T_{o4}} \]

(II.15a) \hspace{1cm} (II.15b)