Lecture # 7

Chemical Thermodynamics 3
Ahmed F. Ghoniem

February 24, 2020

• Adiabatic Combustion
• Gasification
• Availability Loss in adiabatic combustion
• Combustion Engine Efficiency
• Maximum possible efficiency using chemical energy
Equilibrium driven dissociation of H\textsubscript{2}O (top) and of CO\textsubscript{2} (bottom) at high T

Mixtrure has: \( \chi_1, \chi_2, \chi_3, \ldots, \chi_n \)

Some components can participate in one or more reactions:

\[
\sum_{j=1}^{J} v_j \chi_j \Rightarrow \sum_{j=1}^{J} v_j'' \chi_j,
\]

then

\[
\frac{\prod_{j=1}^{J} p_j^{v_j}}{\prod_{j=1}^{J} p_j^{v_j''}} = K_p(T),
\]

where

\[
\sigma = \sum_{\text{prod}} v_j'' - \sum_{\text{react}} v_j
\]

\[
\prod_{\text{prod}} X_j^{v_j} \prod_{\text{react}} X_j^{v_j'} = K_p(T) \frac{p^\sigma}{P^\sigma}
\]

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Adiabatic Combustion of Hydrogen-Oxygen, and their Flame temperature

\[
\phi H_2 + \frac{1}{2} O_2 \Rightarrow \alpha_{H_2} H_2 + \alpha_{O_2} O_2 + \alpha_{H_2O} H_2O
\]

Equilibrium of \( H_2O \Leftrightarrow H_2 + \frac{1}{2} O_2 \)

and + the energy equation ...

\[ \sum n_i \hat{h}_i(T_r) = \sum n_i \hat{h}_i(T_p) \]
Computing products of combustion of HC combustion using equilibrium constants

\[ \phi C_m H_n + \left( m + \frac{n}{4} \right) (O_2 + 3.76N_2) \Rightarrow \]

\[ \alpha_{CO_2} CO_2 + \alpha_{H_2O} H_2 + 3.76 \left( m + \frac{n}{4} \right) N_2 + \alpha_{CO} CO + \alpha_{H_2} H_2 + \alpha_{O_2} O_2 \]

six unknowns (including T):

1. Mass conservation (3 equations) \( m = \alpha_{CO_2} + \alpha_{CO}, \) and \( n = 2 \left( \alpha_{H_2O} + \alpha_{H_2} \right) \)

and \( \left( m + \frac{n}{4} \right) = \alpha_{CO_2} + \frac{1}{2} \alpha_{CO} + \frac{1}{2} \alpha_{H_2O} + \alpha_{O_2} \) (note that: \( X_i = \alpha_i / \sum \alpha_i \))

2. Energy Conservation (constant H): \( \sum_{\text{react}} \nu_i \hat{h}_i(T_1) = \sum_{\text{prod}} \alpha_i \hat{h}_i(T_p) \)

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Important Reactions

3. \( \text{H}_2\text{O} \) Equilibrium: \( \text{H}_2\text{O} \Leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \)

\[
\frac{X_{\text{H}_2}X_{\text{O}_2}^{1/2}}{X_{\text{H}_2\text{O}}} = \frac{K_p}{\sqrt{P}}, \quad K_p(T) = \exp \left( -\frac{\Delta G^o_{\text{R, H}_2\text{O} \Leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2}(T)}{\mathcal{R}T} \right)
\]

4. \( \text{CO}_2 \) Equilibrium: \( \text{CO}_2 \Leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2 \)

\[
\frac{X_{\text{CO}}X_{\text{O}_2}^{1/2}}{X_{\text{CO}_2}} = \frac{K_p}{P^{1/2}}, \quad K_p(T) = \exp \left( -\frac{\Delta G^o_{\text{R, CO}_2 \Leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2}(T)}{\mathcal{R}T} \right)
\]

Methane combustion in air

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If oxygen is not present in products, or is negligible ($\phi \geq 1$) then one reaction is sufficient: Homogeneous water-gas equilibrium:

$$
\begin{align*}
\text{H}_2\text{O} + \text{CO} &\rightleftharpoons \text{H}_2 + \text{CO}_2, \\
\text{and} \quad \frac{X_{\text{H}_2}X_{\text{CO}_2}}{X_{\text{H}_2\text{O}}X_{\text{CO}}} & = K_p,
\end{align*}
$$

with $K_{p,\text{H}_2\text{O}+\text{CO} \rightleftharpoons \text{H}_2+\text{CO}}(T) = $ 

$$
\exp\left(-\frac{\Delta G^o_{R,\text{H}_2\text{O}+\text{CO} \rightleftharpoons \text{H}_2+\text{CO}}(T)}{\mathcal{R}T}\right)
$$

For NO, $\frac{1}{2}\text{O}_2 + \frac{1}{2}\text{N}_2 \rightleftharpoons \text{NO}$, But NO hardly reaches equilibrium.
Coal Gasification and IGCC (also “Clean Coal!”) and pre-combustion CO₂ Capture
## Coal Gasification Reactions

Heating value of coal, 14-35 MJ/kg, or 168-420 MJ/kmol depends on its type

<table>
<thead>
<tr>
<th>Reaction</th>
<th>MJ/kgmol</th>
<th>Conditions</th>
<th>Heat Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial oxidation C+( \frac{1}{2} )O(_2) → CO</td>
<td>-123.1</td>
<td>( \rightarrow ) ( p \uparrow )</td>
<td>Provides gasification heat</td>
</tr>
<tr>
<td>combustion C+O(_2) → CO(_2)</td>
<td>-393.6</td>
<td></td>
<td>Provides more gasification heat</td>
</tr>
<tr>
<td>Boudouard reaction C+CO(_2) → 2CO</td>
<td>159.9</td>
<td>( \rightarrow ) ( p \uparrow ) ( \rightarrow ) ( T \uparrow )</td>
<td>Gasification reaction</td>
</tr>
<tr>
<td>Heterogeneous shift reaction C+H(_2)O → CO +H(_2)</td>
<td>118.5</td>
<td>( \rightarrow ) ( p \uparrow ) ( \rightarrow ) ( T \uparrow )</td>
<td>Gasification reaction</td>
</tr>
<tr>
<td>methane formation C+2H(_2) → CH(_4)</td>
<td>-87.5</td>
<td>( \rightarrow ) ( p \uparrow ) ( \rightarrow ) ( T \uparrow )</td>
<td></td>
</tr>
<tr>
<td>Homogeneous shift reaction CO+H(_2)O → CO(_2) +H(_2)</td>
<td>-40.9</td>
<td>( \rightarrow ) ( T \uparrow )</td>
<td></td>
</tr>
<tr>
<td>Methanation reaction CO+3H(_2) → CH(_4) +H(_2)O</td>
<td>-205.9</td>
<td>( \rightarrow ) ( p \uparrow ) ( \rightarrow ) ( T \uparrow )</td>
<td></td>
</tr>
</tbody>
</table>

- One kmol of CH\(_4\) (LHV=800 MJ/kmol) results in 2 kmol H\(_2\) (total LHV=2x240=480 MJ) and 1 kmol of C (HV=394 MJ) and requires ~ 80 MJ/kmol (difference between the products and reactants total enthalpy).
- Total H\(_2\) energy (480 MJ) is 60% of what we had originally.

Gottlicher, The Energetics of Carbon Dioxide Capture in Power Plants, DOE, 2004

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Because of heat transfer processes and gas separation in synthetic fuel production, system integration is important for raising the overall reforming efficiency ...

\[ \eta_{\text{reform}} = \frac{\text{chemical energy out (+ thermal !)}}{\text{chemical (and thermal) energy in} + \text{separation work}} \]

\[ \frac{\left( \dot{n}_f \Delta h_f \right)_{\text{out}} + \dot{Q}_{\text{out}}}{\sum_{\text{in}} \left( \dot{n}_f \Delta h_f \right) + \dot{Q}_{\text{in}} + \dot{E}_{\text{sep}}} \]

\[ \dot{E}_{\text{sep}} \] should be measured in terms of "heat equivalent"

- High efficiency heat exchangers are needed.
- Cost is high, integration justifiable for large production.
- Less so for local operation or mobile applications.
- Progress and innovation are underway.

### Efficiency of Synthetic Fuel Production

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Product</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>syngas</td>
<td>72-87%</td>
</tr>
<tr>
<td>Coal</td>
<td>methane</td>
<td>61-78%</td>
</tr>
<tr>
<td>Coal</td>
<td>Methanol</td>
<td>51-59%</td>
</tr>
<tr>
<td>Coal</td>
<td>Hydrogen</td>
<td>62%</td>
</tr>
<tr>
<td>Oil</td>
<td>Hydrogen</td>
<td>77%</td>
</tr>
<tr>
<td>Methane</td>
<td>Hydrogen</td>
<td>70-79%</td>
</tr>
<tr>
<td>Coal/Oil/Gas</td>
<td>Hydrogen (E)</td>
<td>20-30%</td>
</tr>
<tr>
<td>Oil Shale</td>
<td>Oil/Gas</td>
<td>66-72%</td>
</tr>
<tr>
<td>Methanol</td>
<td>Oil/gas</td>
<td>86%</td>
</tr>
<tr>
<td>Wood</td>
<td>Gas</td>
<td>90%</td>
</tr>
<tr>
<td>Corn</td>
<td>Ethanol</td>
<td>46%</td>
</tr>
<tr>
<td>Manure</td>
<td>Gas</td>
<td>90%</td>
</tr>
</tbody>
</table>


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1. Chemical energy can be converted to thermal energy or heat at nearly 100% efficiency (some equilibrium limitations).

2. Chemical Energy can be converted to other forms of chemical energy, typically conversion is limited by equilibrium which is $T$ (and $p$) dependent, but at < 100 % due to losses in the system. If other chemicals are produced, separation energy further reduces the output.

3. Chemical energy can be converted to work in
   2. Directly, through electrochemical reaction, nearly isothermally, lowering entropy generation. What is this?
Adiabatic Combustion involves entropy generation and loss of availability, but raises the temperature to values suitable for the operation of heat engines.

For adiabatic reactions:

$$\Delta S_R = \Delta S_g = \sum_{\text{prod mix}} n_i \hat{s}_i(T, p, X_i)$$

$$- \sum_{\text{react mix}} n_i \hat{s}_i(T, p, X_i)$$

OR

$$\Delta S_g = S_p(T_F, p_p) - S_r(T^*, p^*)$$

adiabatic flame temperature, pressure, entropy generation, and composition of some of the product gases for combustion of isooctane, $C_8H_{18}$, in a perfectly insulated constant-volume combustion chamber, Gyftopoulos and Beretta

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$T_b$</th>
<th>$p_b$</th>
<th>$\frac{T_S\text{avg}}{\left( -n_{is} \Delta \tilde{g}^\circ \right)}$</th>
<th>$CO_2$</th>
<th>$CO$</th>
<th>$H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>atm</td>
<td>%</td>
<td>kmol MJ</td>
<td>mol MJ</td>
<td>mol MJ</td>
</tr>
<tr>
<td>1.0</td>
<td>2912</td>
<td>44.8</td>
<td>20.8</td>
<td>1.17</td>
<td>357</td>
<td>73.8</td>
</tr>
<tr>
<td>1.1</td>
<td>2843</td>
<td>43.2</td>
<td>21.5</td>
<td>1.30</td>
<td>230</td>
<td>44.9</td>
</tr>
<tr>
<td>1.2</td>
<td>2758</td>
<td>41.5</td>
<td>22.1</td>
<td>1.39</td>
<td>143</td>
<td>27.6</td>
</tr>
<tr>
<td>1.3</td>
<td>2667</td>
<td>39.9</td>
<td>22.8</td>
<td>1.44</td>
<td>86.8</td>
<td>17.0</td>
</tr>
<tr>
<td>1.4</td>
<td>2577</td>
<td>38.4</td>
<td>23.4</td>
<td>1.48</td>
<td>52.1</td>
<td>10.5</td>
</tr>
<tr>
<td>1.5</td>
<td>2489</td>
<td>37.0</td>
<td>23.9</td>
<td>1.50</td>
<td>31.4</td>
<td>6.60</td>
</tr>
<tr>
<td>1.6</td>
<td>2408</td>
<td>35.7</td>
<td>24.5</td>
<td>1.51</td>
<td>19.0</td>
<td>4.19</td>
</tr>
<tr>
<td>1.7</td>
<td>2332</td>
<td>34.5</td>
<td>25.0</td>
<td>1.52</td>
<td>11.7</td>
<td>2.70</td>
</tr>
<tr>
<td>1.8</td>
<td>2262</td>
<td>33.4</td>
<td>25.4</td>
<td>1.52</td>
<td>7.28</td>
<td>1.78</td>
</tr>
<tr>
<td>1.9</td>
<td>2198</td>
<td>32.4</td>
<td>25.9</td>
<td>1.53</td>
<td>4.61</td>
<td>1.19</td>
</tr>
<tr>
<td>2.0</td>
<td>2138</td>
<td>31.4</td>
<td>26.3</td>
<td>1.53</td>
<td>2.96</td>
<td>0.78</td>
</tr>
</tbody>
</table>

mixture of isooctane and dry air is at $T_a = 700$ K and $p_a = 10$ atm.
Work interaction in a Process undergoing Chemical Reaction

steady state, flow process

\[ Q - W = H_{out} - H_{in} \]

\[ 0 = \frac{Q}{T^*} + S_{in} - S_{out} + \Delta S_g \]

\[ W_{\text{chem.eng.}} = (H_1 - T^* S_1) - (H_2 - T^* S_2) - T^* \Delta S_g \]

(availability-Irreversibility)

reactants at state 1 and products at state 2:

\[ W = \sum_{\text{react}} n_i \left( \hat{h}_i (T_1) - T^* \hat{s}_i (T_1, p_{i,1}) \right) - \sum_{\text{prod}} n_i \left( \hat{h}_i (T_2) - T^* \hat{s}_i (T_2, p_{i,2}) \right) - T^* \Delta S_g \]

Maximum Work, \( \Delta S_g \rightarrow 0 \)

\[ W_{\text{max.chem.eng.}} = \sum_{\text{react},1} v_i (\hat{h}_i - T^* \hat{s}_i) - \sum_{\text{prod},2} v_i (\hat{h}_i - T^* \hat{s}_i) \]

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"Largest" Maximum work:

exit stream at mechanical, thermal
and chemical equilibrium with environment,
If inlet and exit streams are both at
mechanical and thermal equilibrium
with the environment \( (T_o, p_o) = (T^o, p^o) \):

\[
w_{\text{max}} = \sum_{i} v_i \left( h_i (T_o) - T_o \hat{s}_i (T_o, p_o) \right) - \sum_{i} v_i \left( h_i (T_o) - T_o \hat{s}_i (T_o, p_o) \right)
\]

\[
= -\Delta G^o_R (T_o, p_o) = -\Delta G^\text{avail}_R (T_o, p_o)
\]

Since \( p_o = 1 \text{ atm}, \)

\[
\left( -\Delta G^\text{avail}_R \right) = \left( -\Delta G^o_R (T_o) \right) + \Re T_o \ell \ln \left( \prod_{\text{react}} X_i^{v_i} / \prod_{\text{prod}} X_i^{v_i} \right)
\]

\[
\approx \Delta G^o_R
\]

Calculations show that \( \Delta G^o_R \approx \Delta H^o_{R,LHV} \)

<table>
<thead>
<tr>
<th>Fuel (phase)</th>
<th>(-\Delta H^o_R) (for LHV) (kJ/mol)</th>
<th>(-\Delta H^o_R) (for HHV) (kJ/mol)</th>
<th>(-\Delta G^o_R (T^o, p^o)) (kJ/mol)</th>
<th>(\hat{\xi}^o) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (g), H(_2)</td>
<td>241.8</td>
<td>285.9</td>
<td>228.6</td>
<td>235.2</td>
</tr>
<tr>
<td>Carbon (s), C</td>
<td>393.5</td>
<td>393.5</td>
<td>394.4</td>
<td>410.5</td>
</tr>
<tr>
<td>Paraffin (alkane) Family, C(<em>n) H(</em>{2n+2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane (g), CH(_4)</td>
<td>802.3</td>
<td>890.4</td>
<td>818</td>
<td>830.2</td>
</tr>
<tr>
<td>Ethane (g), C(_2)H(_6)</td>
<td>1427.9</td>
<td>1559.9</td>
<td>1467.5</td>
<td>1493.9</td>
</tr>
<tr>
<td>Propane (g), C(_3)H(_8)</td>
<td>2044</td>
<td>2220</td>
<td>2108.4</td>
<td>2149</td>
</tr>
<tr>
<td>Butane (g), C(<em>4)H(</em>{10})</td>
<td>2658.5</td>
<td>2878.5</td>
<td>2747.8</td>
<td>2802.5</td>
</tr>
<tr>
<td>Pentane (g), C(<em>5)H(</em>{12})</td>
<td>3272.1</td>
<td>3536.1</td>
<td>3386.9</td>
<td>3455.8</td>
</tr>
<tr>
<td>Pentane (l), C(<em>5)H(</em>{12})</td>
<td>3245.5</td>
<td>3509.5</td>
<td>3385.8</td>
<td>3454.8</td>
</tr>
<tr>
<td>Hexane (g), C(<em>6)H(</em>{14})</td>
<td>3886.7</td>
<td>4194.8</td>
<td>4026.8</td>
<td>4110</td>
</tr>
<tr>
<td>Hexane (l), C(<em>6)H(</em>{14})</td>
<td>3855.1</td>
<td>4163.1</td>
<td>4022.8</td>
<td>4106</td>
</tr>
<tr>
<td>Heptane (g), C(<em>7)H(</em>{16})</td>
<td>4501.4</td>
<td>4853.5</td>
<td>4667</td>
<td>4764.3</td>
</tr>
<tr>
<td>Heptane (l), C(<em>7)H(</em>{16})</td>
<td>4464.9</td>
<td>4816.9</td>
<td>4660</td>
<td>4757.3</td>
</tr>
<tr>
<td>Octane (g), C(<em>8)H(</em>{18})</td>
<td>5116.2</td>
<td>5512.2</td>
<td>5307.1</td>
<td>5418.6</td>
</tr>
<tr>
<td>Octane (l), C(<em>8)H(</em>{18})</td>
<td>5074.6</td>
<td>5470.7</td>
<td>5297.2</td>
<td>5408.7</td>
</tr>
</tbody>
</table>

\(\hat{\xi}^o\) = \(-\Delta G^o_R\) + \Re T_o \ell \ln \left( \prod_{\text{react} \neq \text{fuel}} X_i^{v_i} / \prod_{\text{prod}} (X_i^o)^{v_i} \right) \approx \left( -\Delta G^o_{R,fuel} \right)

\(X_i^o\) are evaluated for standard concentrations (except for the fuel)


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A Possible Model:

\[
W_{\text{max,comb,eng.}} = W_{\text{max,chem,eng}} - T^* \Delta S_{\text{ad,comb}}
\]

\[
= (H_1 - T^* S_1) - (H_2 - T^* S_2) - T^* \Delta S_g
\]

\[
= (H_F - T^* S_F) - (H_2 - T^* S_2)\quad (= W_{\text{car}}(T_F, T^*))
\]

\[
(\eta_{\text{best,comb}})_{\text{sec Law}} = \frac{W_{\text{max,comb,eng}}}{\Delta G_R^o} - \frac{W^*_{\text{max,chem,eng}}}{\Delta G_R^o} - \frac{T_o \Delta S_{\text{ad,comb}}}{\Delta G_R^o}
\]

\[
\eta_{\text{best,comb}} \approx \frac{W^*_{\text{max,chem,eng}}}{\Delta G_R^o} - \frac{T_o \Delta S_{\text{ad,comb}}}{\Delta G_R^o}
\]

Another model uses:

\[
\eta_{\text{car}} = 1 - \ell n \left( \frac{T_F}{T^*} \right) \left( \frac{T_F}{T^*} - 1 \right)
\]

\[
= 70\% \quad \text{for} \quad T_F / T^* = 8
\]

\[
W_{\text{max}} = \eta_{\text{car}} \left| \Delta H_R \right|
\]

- The choice of \( T_F \) is tricky, its max is the adiabatic stoichiometric flame \( T \), but the actual value depends on the equipment
- Another model uses the log mean temperature Carnot efficiency \( T_F \) and \( T^* \) and enthalpy of reaction for \( \text{max} \ W \).
- Again the choice of \( T_F \) is tricky!

See Tables

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