Heating value, adiabatic flame temperature, air factor
In a boiler fuel is burned (oxidized) to flue gas components. In this process, (chemical) energy is released and bound to the flue gas components. Heat is then removed from the flue gas to heat up water/steam.

The fuel heating value refers to the amount of energy released from the fuel during oxidation (MJ/kg).

For solid fuels, the HV is determined experimentally.

For fuels with well defined chemical structure, the heating value can be calculated from thermodynamic data.
HV of CH₄ from thermodynamic data

\[ \text{1 CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{1 CO}_2(g) + 2 \text{H}_2\text{O}(g) \]

Tabulating data for heat of reaction (HV) for each reaction would require own table for each reaction (~infinite number)

Instead the concept of ”state variable” is utilized, and formation enthalpies for reaction components are tabulated, and can be used to calculate the heat of reaction (HV) for any reaction
HV of CH\textsubscript{4} from thermodynamic data

\[ 1 \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow 1 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \]

Elements

1 C, 4 H, 4 O

Elements at their reference state; most stable state at P=1 bar, T=25 °C

C(s), 2 H\textsubscript{2}(g), 2 O\textsubscript{2}(g)
JANAF tables
( http://kinetics.nist.gov/janaf/ )
HV of CH₄ from thermodynamic data

1 CH₄(g) + 2 O₂(g) → 1 CO₂(g) + 2 H₂O(g)

Agreement (definition) that ΔH°ₜ = 0
JANAF tables

( http://kinetics.nist.gov/janaf/ )
HV of CH\textsubscript{4} from thermodynamic data

\[
1 \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow 1 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

Tabulated $\Delta H_f^\circ$ give the change in enthalpy when formed from elements at their reference state.

Elements

1 C, 4 H, 4 O

Agreement (definition) that $\Delta H_f^\circ = 0$

Elements

At their reference state; most stable state at P=1 bar, T=25 °C
HV of CH\(_4\) from thermodynamic data

\[ 1 \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 1 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \]

Elements

- 1 C, 4 H, 4 O

Elements at their reference state; most stable state at P=1 bar, T=25 °C

\[ \Delta H_f^\circ = 0 \]
JANAF tables

### Carbon Dioxide (CO₂)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Cₚ</th>
<th>S</th>
<th>ΔGₚ (kJ/mol)</th>
<th>ΔHₚ (kJ/mol)</th>
<th>ΔS</th>
<th>log Kₛ₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-393.131</td>
<td>-393.131</td>
<td>INFINITE</td>
<td>INFINITE</td>
</tr>
<tr>
<td>100</td>
<td>29.208</td>
<td>179.009</td>
<td>241.068</td>
<td>-393.208</td>
<td>-393.803</td>
<td>205.839</td>
</tr>
<tr>
<td>200</td>
<td>32.359</td>
<td>199.975</td>
<td>217.046</td>
<td>-393.404</td>
<td>-394.085</td>
<td>102.924</td>
</tr>
<tr>
<td>298.15</td>
<td>37.129</td>
<td>213.795</td>
<td>213.795</td>
<td>0</td>
<td>-393.523</td>
<td>-394.389</td>
</tr>
</tbody>
</table>

### Water (H₂O)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Cₚ</th>
<th>S</th>
<th>ΔGₚ (kJ/mol)</th>
<th>ΔHₚ (kJ/mol)</th>
<th>ΔS</th>
<th>log Kₛ₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-238.921</td>
<td>-238.921</td>
<td>INFINITE</td>
<td>INFINITE</td>
</tr>
<tr>
<td>100</td>
<td>33.299</td>
<td>152.388</td>
<td>218.334</td>
<td>-240.683</td>
<td>-236.384</td>
<td>123.579</td>
</tr>
<tr>
<td>200</td>
<td>33.349</td>
<td>175.480</td>
<td>191.896</td>
<td>-240.900</td>
<td>-223.001</td>
<td>106.792</td>
</tr>
<tr>
<td>298.15</td>
<td>33.590</td>
<td>188.824</td>
<td>188.824</td>
<td>0</td>
<td>-241.826</td>
<td>-228.382</td>
</tr>
</tbody>
</table>

ΔH, ΔS, and log Kₛ₂O₂ values are calculated for each temperature.
HV of CH₄ from thermodynamic data

1 CH₄(g) + 2 O₂(g) → 1 CO₂(g) + 2 H₂O(g)

Tabulated ΔH̅° give the change in enthalpy when formed from elements at their reference state.

Elements

1 C, 4 H, 4 O

Elements

At their reference state; most stable state at P=1 bar, T=25 °C

C(s) 2 H₂(g) 2 O₂(g)

ΔH̅° = 0

C(s) 2 H₂(g) 2 O₂(g)
HV of CH₄ from thermodynamic data

Going either “way” results in same change in state: state 1 to state 2

1 CH₄(g) + 2 O₂(g) → 1 CO₂(g) + 2 H₂O(g)

Tabulated ΔH_f° give the change in enthalpy when formed from elements at their reference state

Elements

1 C, 4 H, 4 O

C(s) 2 H₂(g) 2 O₂(g)

ΔH_f° = 0

C(s) 2 H₂(g) 2 O₂(g)

Elements

At their reference state; most stable state at P=1 bar, T=25 °C
HV of CH₄ from thermodynamic data

Going either "way" results in same change in state: state 1 to state 2

Tabulated ΔH_f° give the change in enthalpy when formed from elements at their reference state.

1 CH₄(g) + 2 O₂(g) → 1 CO₂(g) + 2 H₂O(g)

Reactants
ΔH_f°
C(s) 2 H₂(g) 2 O₂(g)

Note the "direction" of ΔH_f and path to get from state 1 to state 2

Products
ΔH_f°
C(s) 2 H₂(g) 2 O₂(g)
HV of CH$_4$ from thermodynamic data

$HV$ from $\Delta H_f^\circ$ at 25 °C

$1 \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 1 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

$\Delta H_f^\circ \text{(kJ/mol)}$:  
-74.873  
0  
-393.522  
-241.826
HV of CH$_4$ from thermodynamic data

$HV$ from $\Delta H_f^\circ$ at 25 °C

$1$ CH$_4$(g) + $2$ O$_2$(g) $\rightarrow$ $1$ CO$_2$(g) + $2$ H$_2$O(g)

$\Delta H_f^\circ$ (kJ/mol): $-74.873$ $0$ $-393.522$ $-241.826$

$\Delta H_f^\circ$ (kJ): $1 \times -74.873$ $2 \times 0$ $1 \times -393.522$ $2 \times -241.826$

$\Delta H_f^\circ$ RXN (kJ): $-(1 \times -74.873 + 2 \times 0)$ $+(1 \times -393.522 + 2 \times -241.826)$

$\Delta H_f^\circ$ RXN (kJ): $(1 \times -393.522 + 2 \times -241.826) - (1 \times -74.873 + 2 \times 0) = -802.3$
HV of CH₄ from thermodynamic data

HV from $\Delta H_f$ at 25 °C

$$1 \text{ CH}_4(g) + 2 \text{ O}_2(g) \rightarrow 1 \text{ CO}_2(g) + 2 \text{ H}_2\text{O}(g)$$

$\Delta H_f$ (kJ/mol): -74.873 0 -393.522 -241.826

$\Delta H_f$ (kJ): 1 x -74.873 2 x 0 1 x -393.522 2 x -241.826

$\Delta H_f$ RXN (kJ): (1 x -393.522 + 2 x -241.826) - (1 x -74.873 + 2 x 0) = -802.3

For each mole CH₄ that is oxidized, 802.3 kJ energy needs to be removed from system to maintain temperature 25 °C.

HV for CH₄: 802.3 kJ/mol at 25 °C
Background – adiabatic flame temperature

In a boiler fuel is burned (oxidized) to flue gas components. In this process, (chemical) energy is released and bound to the flue gas components. Heat is then removed from the flue gas to heat up water/steam.

Adiabatic (flame) temperature refers to the theoretical, limiting situation where no heat is removed from flue gas; instead all energy released from combustion goes to heat up flue gas components (CO₂, H₂O, O₂, N₂,...)
Adiabatic flame temperature

Above describes situation of complete combustion (all CH$_4$ to CO$_2$ and H$_2$O). T$_{adiabatic}$ applies also in situations of incomplete combustion (deficiency of O$_2$). T$_{adiabatic}$ can also be calculated considering equilibrium/dissociation due to high T (even if enough O$_2$, at high temperature not all C is fully oxidized to CO$_2$).
How to calculate adiabatic flame temperature?

Data needed
1) Energy released from oxidation (HV)
2) Enthalpy of flue gas components at different temperatures (Cp)
3) $T_{init}$

$$E = m \cdot \int Cp \cdot (T_{ad} - T_{init})$$
Adiabatic flame temperature $\text{CH}_4$

JANAF tables
( http://kinetics.nist.gov/janaf/ )

Data needed

1) Energy released from oxidation (HV)

2) Enthalpy of flue gas components at different temperatures (Cp)

3) $T_{\text{init}}$

\[
E = m \cdot \int \Delta H \cdot (T_{\text{ad}} - T_{\text{init}})
\]
Adiabatic flame temperature $\text{CH}_4$

Data needed
1) Energy released from oxidation (HV)
2) Enthalpy of flue gas components at different temperatures (Cp)
3) $T_{\text{init}}$

\[ E = m \cdot \int \text{Cp} \cdot (T_{\text{ad}} - T_{\text{init}}) \]
Adiabatic flame temperature CH₄

Data needed

1) Energy released from oxidation (HV)
2) Enthalpy of flue gas components at different temperatures (Cp)
3) $T_{\text{init}}$

$$E = m \cdot \int Cp \cdot (T_{\text{ad}} - T_{\text{init}})$$
Adiabatic flame temperature CH$_4$

\[1\text{CH}_4 + 2\text{O}_2 \rightarrow 1\text{CO}_2 + 2\text{H}_2\text{O}\]

**Data needed**

1) Energy released from oxidation (HV)
2) Enthalpy of flue gas components at different temperatures (Cp)
3) \(T_{init}\)

\[E = m \cdot \int C_p \cdot (T_{ad} - T_{init})\]
Adiabatic flame temperature CH₄

1CH₄ + 2O₂ → 1CO₂ + 2H₂O

Data needed

1) Energy released from oxidation (HV)
2) Enthalpy of flue gas components at different temperatures (Cp)
3) T.Init

\[ E = m \cdot \int_{Cp} \cdot (T_{ad} - T_{init}) \]
Air factor ($\lambda$)

\[ \begin{align*}
1\text{CH}_4 + 2\text{O}_2 & \rightarrow 1\text{CO}_2 + 2\text{H}_2\text{O} \\
1\text{CH}_4 + 1\text{O}_2 & \rightarrow ? \\
1\text{CH}_4 + 3\text{O}_2 & \rightarrow ?
\end{align*} \]

Air factor ($\lambda$) = \[ \frac{\text{Air (oxidizer)}}{\text{Fuel}} \]

\[ \frac{\text{Stoichiometric air (oxidizer)}}{\text{Fuel}} \]

Air-to-fuel ratio in e.g. a boiler or a boiler section

Air-to-fuel ratio at which just enough oxygen to oxidize fuel completely; see top-most reaction equation.
Air factor ($\lambda$)

$\lambda \geq 1$, "oxidizing conditions"
$\lambda < 1$, "reducing conditions"

Air factor ($\lambda$) = \[
\frac{\text{Air (oxidizer)}}{\text{Fuel}} - \frac{\text{Stoichiometric air (oxidizer)}}{\text{Fuel}} = \frac{\text{Air (oxidizer)}}{\text{Stoichiometric air (oxidizer)}}
\]