

# Equilibrium

## 1 Equilibrium

### 1.1 Chemical Thermodynamics

In chemical thermodynamics, we calculate the final (product) properties based on the initial (reactant) state and information during the process, assuming the thermodynamic equilibrium achieved. Normally we calculate the properties using first and second thermodynamics law and mass (atom) conservation.

### 1.2 Equilibrium and Kinetics

Equilibrium considers where reaction is heading to if given enough time, kinetics considers chemical rates, which means how fast a reaction occurs as it tends toward equilibrium.

## 2 Equivalence Ratio

Define the initial reactant composition in terms of fuel-oxidizer ratio  $f$ :

$$f = \frac{\text{mass fuel}}{\text{mass oxidizer}} \quad (1)$$

$$f = \frac{\text{moles fuel}}{\text{moles oxidizer}} \quad (2)$$

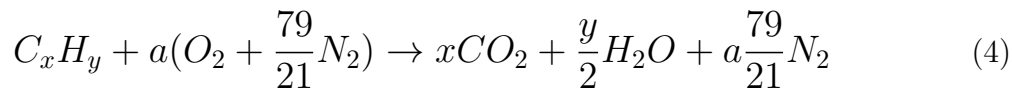
Then, we define the equivalence ratio as:

$$\phi = \frac{f_{actual}}{f_{stoichiometric}} \quad (3)$$

Notice that:

1.  $\phi = 1$ : Stoichiometric, just enough oxidizer to completely consume fuel
2.  $\phi < 1$ : fuel lean, excess oxidizer
3.  $\phi > 1$ : fuel rich, excess fuel

We define the synthetic air as 79%  $N_2$  and 21%  $O_2$ . Then, at stoichiometric condition:



$$a = x + y/4 \quad (5)$$

## 3 Adiabatic Flame Temperature

### 3.1 Definition

Equilibrium temperature that would be achieved if reactants were converted to equilibrium products without external heat addition or loss.

### 3.2 Constant Pressure

From first thermodynamics law:

$$dU = \delta Q + \delta W \quad (6)$$

Here:

1.  $dU$  is the change of internal energy
2.  $\delta Q$  is the heat quantity **into** the system
3.  $\delta W$  is the work done **into** the system

Consider the work only contains compression work, then:

$$\delta W = -pdV \quad (7)$$

The negative sign means that when the flow is compressed (volume decreases), there is a positive work done into the system.

Also, because we assume the system is adiabatic:

$$\delta Q = 0 \quad (8)$$

When the pressure is constant:

$$dU = -pdV \quad (9)$$

Or based on the definition of enthalpy:

$$dH = 0 \quad (10)$$

Therefore,

$$h_{react}(T, P) = h_{prod}(T, P) \quad (11)$$

$$\sum_{i=react} h_i Y_i = \sum_{j=prod} h_j Y_j \quad (12)$$

Where  $Y_i$  is the mass fraction and:

$$h_i(T) = [h_T - h_{T_{ref}}]_i + [\Delta h_{f,T_{ref}}^\circ]_i \quad (13)$$

Where  $[\Delta h_{f,T_{ref}}^\circ]_i$  refers to enthalpy of formation, and the sensible enthalpy is defined as:

$$h_T - h_{T_{ref}} = \int_{T_{ref}}^T C_p(T') dT' \quad (14)$$

Plug back in, we get:

$$\sum_j Y_j [(h_{T_{ad}} - h_{T_{ref}}) + \Delta h_{f,T_{ref}}^\circ]_j = \sum_i Y_i [(h_{T_{react}} - h_{T_{ref}}) + \Delta h_{f,T_{ref}}^\circ]_i \quad (15)$$

$$\underbrace{\sum_j Y_j [(h_{T_{ad}} - h_{T_{ref}})]_j}_{\text{Prod Sensible h}} = \underbrace{\sum_i Y_i [(h_{T_{react}} - h_{T_{ref}})]_i}_{\text{React Sensible h}} + \underbrace{\sum_i Y_i [\Delta h_{f,T_{ref}}^\circ]_i - \sum_j Y_j [\Delta h_{f,T_{ref}}^\circ]_j}_{\text{Chemical Energy Conversion at ref T}} \quad (16)$$

### 3.3 Constant Volume

Similar with constant pressure, now:

$$dU = 0 \quad (17)$$

$$U_{react}(T, P) = U_{prod}(T, P) \quad (18)$$

$$U = H - PV \quad (19)$$

$$H_{react} - H_{prod} - V(P_i - P_f) = 0 \quad (20)$$

Assume ideal gas, then:

$$P_i V = \sum_{i=react} N_{react} R T_{react} \quad (21)$$

$$P_f V = \sum_{i=prod} N_{prod} R T_{prod} \quad (22)$$

$$H_{react} - H_{prod} - R(N_{react} T_{react} - N_{prod} T_{ad}) = 0 \quad (23)$$

The following steps are the same as constant pressure case.

### 3.4 Typical Stoichiometric Adiabatic Temperature

## Typical Stoichiometric $T_{ad}$

$p=1 \text{ atm}$ ,  $T_{react}=298 \text{ K}$ , oxidizer=air

Fuel	$T_{ad} \text{ (K) at } \phi=1$
<b>Methane</b> $\text{CH}_4$	2220
<b>Propane</b> $\text{C}_3\text{H}_8$	2260
<b>n-Octane</b> $\text{n-C}_8\text{H}_{18}$	2270
<b>Propylene</b> (propene) $\text{C}_3\text{H}_6$	2330
<b>Ethylene</b> (ethene) $\text{C}_2\text{H}_4$	2370
<b>Hydrogen</b> $\text{H}_2$	2380
<b>Carbon Monoxide</b> $\text{CO}$	2380
<b>Acetylene</b> (ethyne) $\text{C}_2\text{H}_2$	2540

### 3.5 Adiabatic Temperature Dependence

#### 3.5.1 Pressure

Dissociation causes a lowering of the adiabatic temperature since more energy is tied up in chemical bonds (enthalpy of formation) at the expense of the sensible enthalpy. As we increase the pressure, we decrease dissociation (Le chatelier's principle: dissociation tends to increase molecules, which will increase pressure.) and, therefore we increase the adiabatic flame temperature.

#### 3.5.2 Temperature

The adiabatic flame temperature increases as we increase the initial temperature. This is a direct result from the enthalpy conservation. However, as we increase the inlet temperature and the final temperature also increases, the dissociation also increases, distributing some energy. Therefore the corresponding increase in final temperature is not the same as (lower than) in the initial temperature.

#### 3.5.3 Activation Energy

The adiabatic flame temperature is calculated based on the assumption that the thermodynamic equilibrium has been achieved. The activation energy gives us information about the reaction rates. Therefore, the activation energy does not have influence

on adiabatic flame temperature calculations. It will depend only on initial and final states and not on the path or how long it takes to reach equilibrium.

### 3.5.4 Equivalence Ratio

For most of the hydrocarbon fuels, the maximum adiabatic flame temperature occurs at slightly rich equivalence ratio, for two reasons:

1. **Heat Capacity:** A rich mixture has additional fuel beyond what is required for complete combustion. This excess fuel, unburned, serves as a thermal sink, absorbing some of the heat of the reaction. Even though this seems counterintuitive, the key point is that the specific heat capacity (the amount of heat per unit mass required to raise the temperature by one degree) of typical hydrocarbon fuels is lower than that of the combustion products such as CO<sub>2</sub> and H<sub>2</sub>O. This means that the excess fuel in a rich mixture can absorb heat and increase in temperature more readily than the equivalent mass of combustion products in a lean mixture.
2. **Dissociation:** At high temperatures, combustion products (like CO<sub>2</sub> and H<sub>2</sub>O) can start to dissociate, breaking apart into their constituent atoms (like C, O, H). This process absorbs heat, lowering the flame temperature. When the mixture is stoichiometric (chemically balanced), all the fuel and oxygen are consumed to produce combustion products, which then dissociate at high temperatures. But in a rich mixture, the excess fuel 'consumes' some of this dissociation energy, reducing the extent of dissociation and thus increasing the flame temperature.

## 4 Heating Value

Heating value is the energy obtainable by burning one unit of fuel (e.g., 1 kg or kmol) in defined oxidizer at fixed T assuming "ideal" products (e.g., CO<sub>2</sub>, H<sub>2</sub>O). On per mass basis:

$$HV = \frac{H_{react}(T_{ref}) - H_{prod}(T_{ref})}{m_{fuel}} \quad (24)$$

$$HV = \frac{\sum_i Y_i [\Delta h_{f,T_{ref}}]_i - \sum_j Y_j [\Delta h_{f,T_{ref}}]_j}{Y_{fuel}} \quad (25)$$

Typical LHV's:

• **Typical LHV (air, 298K)** (LowerHV=H<sub>2</sub>O vapor in products)

Fuel	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>12</sub> H <sub>26</sub>	CO
LHV (MJ/kg)	120	50	50	47	46	44	10