§ Notions on some frequently used definitions

① Equivalence Ratio : $\phi = \dfrac{F/O}{(F/O)_{st}} = \dfrac{(O/F)_{st}}{O/F}$

> F: Fuel
> O: Oxidizer.

where : F/O is the **mass ratio** of fuel and oxidizer, indicates the mass of fuel required when unit mass of oxidizer is provided.

O/F is the **mass ratio** of Oxider and Fuel, indicates the mass of oxidizer required when unit mass of fuel is provided.

$(\ )_{st}$ indicates the stoichiometric condition.

Usage of ϕ :

when $\phi > 1$, so called Rich Burning, means that the fuel provided is more than what is required in stoichiometric condition.

when $\phi < 1$, so called Lean Burning, means that the fuel provided is less than what is required under stoichiometric condition.

'F/O' is much more frequently used rather than 'O/F' as 'O/F' is a small fraction usually.

② Mixture Fraction :

General meanig : $Z = \dfrac{\text{mass originates from fuel}}{\text{mass of the mixture}}$.

Definition of Z can be provided in different ways:

$1°$ In terms of elements:

$$Z_i = \sum_{k=1}^{N} U_{ik} Y_k$$

$$Z_j = \sum_{k=1}^{N} U_{jk} Y_k.$$

> U_{ik}: the mass ratio of the i-th element in the k-th component.

$$Z \overset{\Delta}{=} \frac{Z_i - Z_i^{(2)}}{Z_i^{(1)} - Z_i^{(2)}} \overset{\Delta}{=} \frac{Z_j - Z_j^{(2)}}{Z_j^{(1)} - Z_j^{(2)}} \quad \text{(Independent of element be choose}$$

(1: Fuel side, 2: Oxidizer side)

2° In terms of mass flux: (Much more frequently used!)

$$z \triangleq \frac{\dot{m}_1}{\dot{m}_1 + \dot{m}_2}$$

For detailed expression of this definition:

$$\frac{dn_i}{\nu_i} = \frac{dn_j}{\nu_j} \quad \text{(since change of mole of each specise is proportionate to its stoichiometric coefficients.)}$$

$$n_i = \frac{Y_i}{W_i} \quad \text{(Relation between mass fraction and molar fraction}$$

$$\Rightarrow \frac{dY_i}{\nu_i W_i} = \frac{dY_j}{\nu_j W_j}$$

Take $i = O_2$ and $j = Fuel$, integrate from unburned status:

$$\frac{Y_{O_2} - Y_{O_2, u}}{\nu_{O_2} W_{O_2}} = \frac{Y_F - Y_{F, u}}{\nu_F W_F}$$

Q: what's $Y_{O_2, u}$ and $Y_{F, u}$? Express them in terms of z?

A: Suppose the mixture is 1kg, then the fuel stream is z (kg) and Oxidizer is $(1-z)$ (kg). Generally, not all the mass in Fuel stream is fuel, so the real fuel mass is $Y_F^{(1)} \times z$ (kg), where $Y_F^{(1)}$ indicates the proportion of real fuel in the fuel stream. Similarly, the real mass of oxidizer is $Y_{O_2}^{(2)} \times (1-z)$ (kg). where $Y_{O_2}^{(2)}$ indicates the proportion of real oxidizer in the oxidizer stream.

Thus: $Y_{O_2, u} = Y_{O_2}^{(2)} (1-z)$; ($Y_{O_2}^{(2)} \doteq 0.232$ when the oxidizer stream is air)

$$Y_{F, u} = Y_F^{(1)} z$$

Substitude these equations into above, yields:
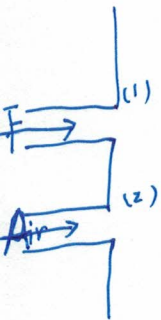
$$\nu Y_F - Y_{O_2} = \nu Y_{F,u} - Y_{O_2,u}.$$

$$= \nu Y_F^{(1)} \cdot Z - Y_{O_2}^{(2)} (1-Z)$$

$$\Rightarrow \quad \boxed{Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2}^{(2)}}{\nu Y_F^{(1)} + Y_{O_2}^{(2)}}}$$

$\left(\nu \triangleq \dfrac{\nu_{O_2} W_{O_2}}{\nu_F \cdot W_F}, \text{ mass ratio of oxidizer and fuel at stoichiometric condition} \right).$

For example, for methane-air case:

$Y_F^{(1)} = 1$ as the fuel stream is pure CH_4.

$Y_{O_2}^{(2)} = 0.232$ as O_2 takes 21% volumetric ratio of air.

$$\nu = \frac{2 \cdot 32}{1 \cdot 16} = 4$$

A typical case for Z is the stoichiometric condition. In this case, the fuel and oxidizer are all consumed completely, thus: $\nu Y_F - Y_{O_2} = 0$.

$$\text{So: } Z_{st} = \frac{Y_{O_2}^{(2)}}{\nu Y_F^{(1)} + Y_{O_2}^{(2)}} = \left(1 + \nu \frac{Y_F^{(1)}}{Y_{O_2}^{(2)}} \right)^{-1}$$

Again, take the methane-air case for example:

$$Z_{st} = \left(1 + 4 \frac{1}{0.232} \right)^{-1} \doteq 0.055.$$

§ Further notions on Z_{st} and remarks on HW2

Q: Given Z, what's the mass fraction of each component before and after burning? Y_i.

A: 1° Y_i for unburned status is trivial.

2° Y_i for burned status need to be discussed for different Z!

(1) $Z \geqslant Z_{st}$: Fuel Rich

(2) $Z < Z_{st}$: Fuel Lean

$\Rightarrow$ different production!

For general combustion case:

$$C_mH_n + (m + \frac{n}{4})O_2 \longrightarrow m\,CO_2 + \frac{n}{2}H_2O$$

when $Z \geqslant Z_{st}$:

$$Y_F = Y_F^{(1)} \frac{Z - Z_{st}}{1 - Z_{st}}$$

$$Y_{O_2} = 0$$

$$Y_{CO_2} = Y_{CO_2, st} \cdot \frac{1 - Z}{1 - Z_{st}}$$

$$Y_{H_2O} = Y_{H_2O, st} \frac{1 - Z}{1 - Z_{st}}$$

when $Z \leq Z_{st}$:

$$Y_F = 0$$

$$Y_{O_2} = Y_{O_2}^{(2)} \cdot (1 - \frac{Z}{Z_{st}})$$

$$Y_{CO_2} = Y_{CO_2, st} \cdot \frac{Z}{Z_{st}}$$

$$Y_{H_2O} = Y_{H_2O, st} \frac{Z}{Z_{st}}$$

where $Y_{CO_2, st}$ and $Y_{H_2O, st}$ are defined as:

$$Y_{CO_2, st} = \cdot Y_F^{(1)} \cdot Z_{st} \cdot \frac{m \cdot W_{CO_2}}{W_F}$$

$$Y_{H_2O, st} = Y_F^{(1)} \cdot Z_{st} \cdot \frac{n \cdot W_{H_2O}}{2 \cdot W_F}$$

The physical meanings of $Y_{CO_2, st}$ and $Y_{H_2O, st}$ is quite clear!

Caution: DO NOT miss N_2 when using air!

Q: Calculate the equivalence ratio in terms of Z?

A: $\phi = \frac{Z}{1 - Z}(\frac{1 - Z_{st}}{Z_{st}})$

§ Chemical reactions:

*. General Form

Suppose there're $\underline{N_R}$ elementary reactions involving $\underline{\underline{N}}$ species:

$$\sum_{m=1}^{N} \nu'_{\ell m} C_m \underset{k_{b\ell}}{\overset{k_{f\ell}}{\rightleftarrows}} \sum_{m=1}^{N} \nu''_{\ell m} C_m \quad (\text{for } \ell = 1, 2, \cdots, N_R)$$

where $\boxed{\nu'_{\ell m}}$ and $\boxed{\nu''_{\ell m}}$ are stoichiometric coefficients corresponding to the m-th species in the ℓ-th forward and backward reaction.

* Reaction rate:

The Arrhenius formulas are the most frequently used form:

$$k_f = A_f T^{B_f} e^{-E_f / R_u T}$$

$$k_b = A_b T^{B_b} e^{-E_b / R_u T}$$

where $\boxed{A_f}$ and $\boxed{A_b}$ are Arrhenius coefficients, $\boxed{E_f}$ and $\boxed{E_b}$ represents the activation energy. $\boxed{B_f}$ and $\boxed{B_b}$ are constants empirically indicating the reaction order.

Thus, the rate of change of molar concentration of species m by the ℓ-th reaction is given by:

$$\dot{C}_m = (\nu''_{\ell m} - \nu'_{\ell m}) \left(k_{f\ell} \prod_{n=1}^{N} C_n^{\nu'_{\ell n}} - k_{b\ell} \prod_{n=1}^{N} C_n^{\nu''_{\ell n}} \right)$$

Hence, the total rate of change of m-th species is:

$$\dot{S}_m = W_m \sum_{\ell=1}^{N_R} \dot{C}_{\ell m}$$

> In chain reactions, the S_m of radicals (or intermediate material) can be assumed to be 0 at statical stationary stat, so that some useful relation can be obtained!

It should be pointed out that not all reaction rate behave in the Arrhenius form! Be careful in practise!

* Adiabatic Flame Temperature & HW2.

Basic principle : Energy Conservation · (As adiabatic means no heat loss,

Different configurations:

1° $p = const$: $\underline{h_u = h_b}$ (The flow work should be considered,

2° $V = const$: $h_u = e_b$ (No flow work)

Take $p = const$ for example:

$$h(T) = \sum_{i=1}^{N} Y_i \cdot h_i(T)$$

In practise, $h_i(T)$ can be calculated by $\underline{looking\text{-}up\ table}$, $\underline{interpolation}$,
or $\underline{integrate\ from\ C_{p,i}}$ ($h_i(T) = h_{i,f} + \int_{Tref}^{T} C_{p,i}(T)\,dT$).

$\underline{h_u}$ is the $\underline{total\ enthalpy\ at\ unburned\ state}$, which can be calculated
easily, to determine T, some numerical algorithm can be employed to
do the $\underline{root\text{-}finding}$ job.

In the example code I provided, the $\underline{Newton\text{-}Iteration}$ is used,
where an initial guess of T should be provided.

For methane - air case, the $Tad - Z$ plot is given as:

Methane-Air Case
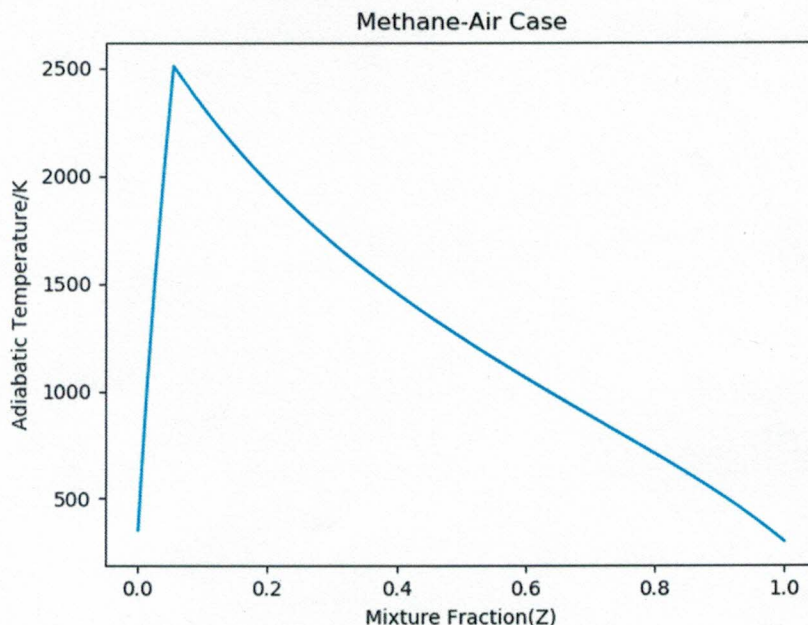
*· Chemical Equilibrium

Determine the <u>direction</u> and <u>extent</u> of chemical reaction by the 2nd law of thermodynamics.

When $T = const$, there're 2 commonly encountered cases:

$1°$ $V = const$:

$$dE = \delta Q - \delta w = dU$$

$$T dS - \delta Q = d(TS) - dU = d(TS - U) \triangleq dA \leq 0$$

$A = TS - U$
Helmholtz Free Energy

$2°$ $P = const$:

$$\delta Q = dw + dU = d(PV) + dU = dH$$

$$T dS - \delta Q = d(TS - H) \triangleq dG \leq 0$$
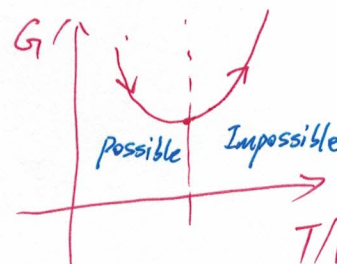
$G = TS - H$
Gibbs Free Energy

Usually, the T and P are <u>pre-fixed in combustion problems</u>, so the gibbs free energy is much more frequently used!

Understand Gibbs Free Energy physically:

The potential to put forward the reaction!

G is always decreasing!

Possible   Impossible

$T/$

Formulas for G:

$$G(P, T) = H(T) - T \cdot S(P, T)$$

$$G - G_0 = (H - H_0) - T(S - S_0)$$

H_0, G_0, S_0: Quantity at <u>reference state.</u>

when ideal gas is employed: $g = g° + TR \ln \frac{P}{P_0}$ (isentropic relation)

Consider multi-component system:

$$G = \sum_{i=1}^{N} N_i g_i \Rightarrow dG = \sum dN_i \cdot g_i + \sum N_i \cdot dg_i$$

$$= \sum dN_i g_i \quad (T = const, \ p = const)$$

$$= \sum \nu_i \cdot g_i \cdot d\varepsilon \quad (dN_i = \nu_i \cdot d\varepsilon, \text{ the extent of react})$$

with $dG = 0$ (The Equilibrim point).

$$\sum_{i=1}^{N} \nu_i g_i \, d\varepsilon = 0$$

$$\Leftrightarrow \quad \sum_{i=1}^{N} \nu_i g_i = 0$$

$$\Leftrightarrow \quad \sum_{i=1}^{N} \nu_i g_i^{(0)} = -\sum_{i=1}^{N} TR \ln\left(\frac{P_i}{P_0}\right)^{\nu_i} = const. \quad \Rightarrow \text{ determine the Temperature.}$$

$$\left(\Rightarrow \quad \prod_{i=1}^{N} \left(\frac{P_i}{P_0}\right)^{\nu_i} = const \quad \text{when } T \text{ is given, as } \sum_{i=1}^{N} \ln\left(\frac{P_i}{P_0}\right)^{\nu_i} = -\frac{\sum_{i=1}^{N} \nu_i g_i^{(0)}}{TR} \right)$$