Chemical Equilibrium

- In general the combustion products consist of more than just CO_2, H_2O, O_2, and N_2
- For rich mixtures CO also exists in the products and at high temperatures the molecules dissociate to form H, O, OH, NO via the following reactions:

$$H_2 \rightarrow 2H \qquad O_2 \rightarrow 2O \qquad H_2 + O_2 \rightarrow 2OH \qquad O_2 + N_2 \rightarrow 2NO$$

- The opposite direction reactions are also possible

$$2H \rightarrow H_2 \qquad 2O \rightarrow O_2 \qquad 2OH \rightarrow H_2 + O_2 \qquad 2NO \rightarrow O_2 + N_2$$

- At **equilibrium** the rate of the forward reaction equals the rate of the backward reaction.

$$H_2 \leftrightarrow 2H \qquad O_2 \leftrightarrow 2O \qquad H_2 + O_2 \leftrightarrow 2OH \qquad O_2 + N_2 \leftrightarrow 2NO$$

Chemical Equilibrium

- At equilibrium the relative proportion of the species mole fraction is fixed

- For the general equilibrium reaction

$$n_A A + n_B B \leftrightarrow n_c C + n_D D$$

- The equilibrium composition for species A, B, C, D is given by:

$$K(T) = \frac{X_C^{n_C} \cdot X_D^{n_D}}{X_A^{n_A} \cdot X_B^{n_B}} \left(\frac{P}{P_{ref}} \right)^{n_C + n_D - n_A - n_B}$$

where K is the **equilibrium constant** which is tabulated as a function of temperature for different equilibrium reactions, P_{ref} is 1 atm and P is in units of atmospheres.

$$Note \quad X_A = \frac{n_A}{n_A + n_B + n_C + n_D}$$

Chemical Equilibrium

Recall that for a rich mixture (γ<1) the reaction equation could not be balanced (5 unknowns a, b, d, e, f and only 4 atom balance equations for C,H,O,N) even if we neglect dissociation (i.e., low product temperature)

$$C_\alpha H_\beta + \gamma(\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + dN_2 + eCO + fH_2$$

If the product species CO_2, H_2O, CO and H_2 are at equilibrium and described by the **water-gas reaction**:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

The equilibrium constant for this reaction provides the fifth equation :

$$K(T) = \frac{X_{CO} \cdot X_{H_2O}}{X_{CO_2} \cdot X_{H_2}} = \frac{e \cdot b}{a \cdot f} \qquad P = 1\,\text{atm}$$

Note K is tabulated as a function of T

Chemical Equilibrium (example)

1 kmol of CO_2, ½ kmol of O_2 and ½ kmol of N_2 reacts to form a mixture consisting of CO_2, CO, O_2, N_2 and NO at 3000K and 1 atm. Determine the equilibrium composition of the product mixture.

$$CO_2 + 1/2 O_2 + 1/2 N_2 \rightarrow \underbrace{aCO + bNO + cCO_2 + dO_2 + eN_2}_{\text{3000K and 1 atm}}$$

C	$1 = a + c$	$c = 1 - a$
O	$3 = a + b + 2c + 2d$	$d = 1/2(1 + a - b)$
N	$1 = b + 2e$	$e = 1/2(1 - b)$

Have 2 unknowns a, b so need 2 equilibrium equations

1. $CO_2 \leftrightarrow CO + 1/2 O_2 \qquad K_1(3000K)$

2. $1/2 O_2 + 1/2 N_2 \leftrightarrow NO \qquad K_2(3000K)$

Chemical Equilibrium (example)

From the equilibrium constant expression

$$K_1 = 0.3273 = \frac{X_{CO} \cdot X_{O_2}^{1/2}}{X_{CO_2}}$$

$$n_{tot} = a+b+c+d+e = a+b+(1-a)+1/2(1+a-b)+1/2(1-b) = (4+a)/2$$

$$X_{CO} = \frac{a}{(4+a)/2} \qquad X_{O_2} = \frac{1/2(1+a-b)}{(4+a)/2} \qquad X_{CO_2} = \frac{1-a}{(4+a)/2}$$

Substituting yields:

$$K_1 = 0.3273 = \frac{X_{CO} \cdot X_{O_2}^{1/2}}{X_{CO_2}} = \frac{a}{1-a}\left(\frac{1+a-b}{4+a}\right)^{1/2} \qquad (1)$$

Chemical Equilibrium (example)

Similarly for the second equilibrium reaction

$$K_2 = 0.1222 = \frac{X_{NO}}{X_{O_2}^{1/2} \cdot X_{N_2}^{1/2}} = \frac{2b}{\left[(1+a-b)(1-b)\right]^{1/2}} \qquad (2)$$

Solving equations 1 and 2 yields:

$a = 0.3745 \quad b = 0.0675$

From the atom balance equations get:

$c = 0.6255 \quad d = 0.6535 \quad e = 0.4663$

Role of Equilibrium Solvers

- If the products are at high temperature (>2000K) minor species will be present due to the dissociation of the major species CO_2, H_2O, N_2 and O_2.

$$C_\alpha H_\beta + (\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2 + eCO + fH_2$$
$$+ gH + hO + iOH + jNO + kN + \cdots$$

- Hand calculations are not practical when many species are considered, one uses a computer program to calculate product equilibrium composition.

Composition of Octane-air Mixtures at Equilibrium