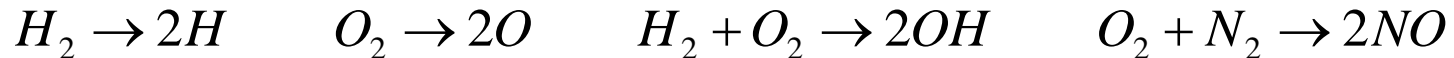


Chemical Equilibrium

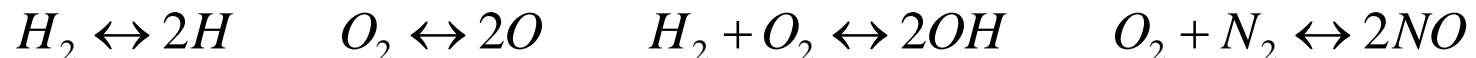
- In general the combustion products consist of more than just CO_2 , H_2O , O_2 , and N_2
- For rich mixtures CO also exists in the products and at high temperatures the molecules dissociate to form H , O , OH , NO via the following reactions:



- The opposite direction reactions are also possible

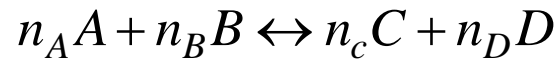


- At **equilibrium** the rate of the forward reaction equals the rate of the backward reaction.



Chemical Equilibrium

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



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

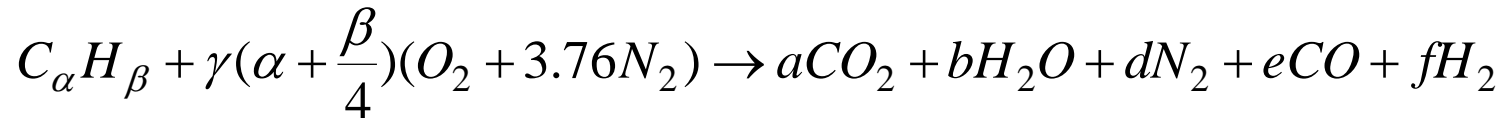
$$K(T) = \frac{X_C^{n_C} \cdot X_D^{n_D}}{X_A^{n_A} \cdot X_B^{n_B}} \left(\frac{P}{P_{ref}} \right)^{n_C + n_D - n_A - n_B}$$

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.

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

Chemical Equilibrium

Recall that for a rich mixture ($\gamma < 1$) 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)



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



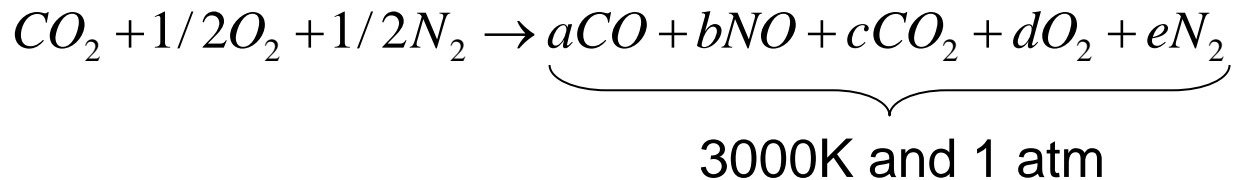
The equilibrium constant for this reaction provides the fifth equation :

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

Note K is tabulated as a function of T

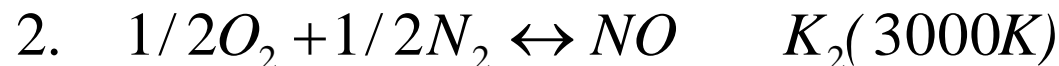
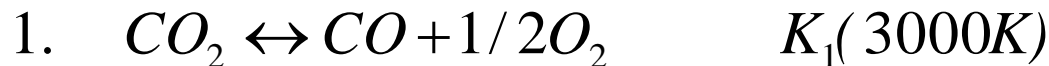
Chemical Equilibrium (example)

1 kmol of CO_2 , $\frac{1}{2}$ kmol of O_2 and $\frac{1}{2}$ 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.



$$\begin{array}{ll} C & 1 = a + c \qquad c = 1 - a \\ O & 3 = a + b + 2c + 2d \qquad d = 1/2(1 + a - b) \\ N & 1 = b + 2e \qquad e = 1/2(1 - b) \end{array}$$

Have 2 unknowns a, b so need 2 equilibrium equations



Chemical Equilibrium (example)

From the equilibrium constant expression

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

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

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

Substituting yields:

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

Chemical Equilibrium (example)

Similarly for the second equilibrium reaction

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

Solving equations 1 and 2 yields:

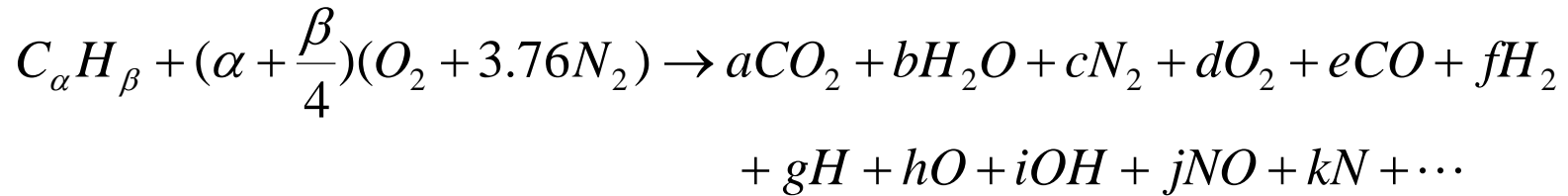
$$a = 0.3745 \quad b = 0.0675$$

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 .



- 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

