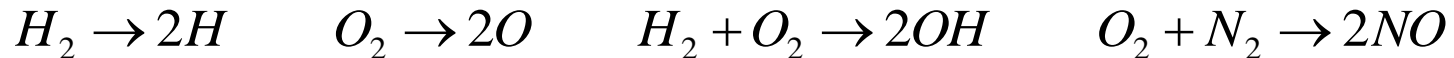# *Fuel & Advanced Combustion*

Lecture 3
Combustion Equilibrium

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. 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.

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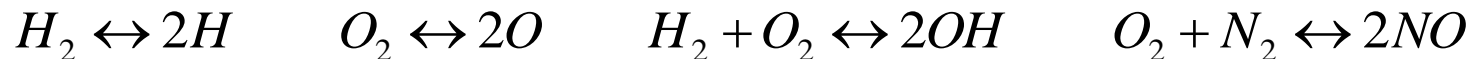
Chemical Equilibrium

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

For the general equilibrium reaction

$$n_A A + n_B B \leftrightarrow n_c C + n_D D$$
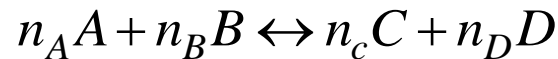
The equilibrium composition for species A, B, C, D is given by:

$$K(T) = \frac{Y_C^{n_C} \cdot Y_D^{n_D}}{Y_A^{n_A} \cdot Y_B^{n_B}} \left(\frac{P}{P_{ref}} \right)^{n_C + n_D - n_A - n_B}$$

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.

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

Equilibrium Constants

(A) $H_2 \rightarrow 2H$
(B) $N_2 \rightarrow 2N$
(C) $O_2 \rightarrow 2O$
(D) $CO_2 \rightarrow CO + \frac{1}{2}O_2$
(E) $H_2O \rightarrow OH + \frac{1}{2}H_2$
(F) $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$
(G) $CO_2 + H_2 \rightarrow CO + H_2O$ ← water gas reaction

T (K)	(A)	(B)	(C)	(D)	(E)	(F)	(G)	T (K)
298.15	−71.30	−159.7	−81.28	−45.05	−46.10	−15.15	−4.950	298.15
300	−70.83	−158.7	−80.73	−44.74	−45.80	−15.07	−4.905	300
400	−51.73	−117.4	−58.91	−32.43	−33.48	−11.14	−3.215	400
500	−40.26	−92.63	−45.82	−25.03	−26.09	−8.784	−2.193	500
600	−32.62	−76.12	−37.10	−20.10	−21.16	−7.210	−1.506	600
700	−27.16	−64.33	−30.86	−16.57	−17.64	−6.086	−1.014	700
800	−23.06	−55.48	−26.19	−13.92	−15.00	−5.243	−0.642	800
900	−19.88	−48.60	−22.55	−11.86	−12.95	−4.587	−0.352	900
1000	−17.33	−43.10	−19.64	−10.21	−11.31	−4.063	−0.120	1000
1100	−15.18	−38.54	−17.21	−8.843	−9.922	−3.633	0.040	1100
1200	−13.40	−34.75	−15.20	−7.739	−8.784	−3.275	0.152	1200
1300	−11.89	−31.54	−13.49	−6.802	−7.821	−2.972	0.251	1300
1400	−10.60	−28.79	−12.03	−6.004	−6.996	−2.712	0.330	1400
1500	−9.474	−26.41	−10.76	−5.315	−6.280	−2.487	0.397	1500
1600	−8.492	−24.32	−9.657	−4.711	−5.654	−2.290	0.456	1600
1700	−7.626	−22.48	−8.680	−4.175	−5.102	−2.116	0.510	1700
1800	−6.856	−20.85	−7.811	−3.697	−4.611	−1.962	0.560	1800
1900	−6.168	−19.39	−7.033	−3.268	−4.172	−1.824	0.608	1900
2000	−5.548	−18.07	−6.334	−2.879	−3.777	−1.699	0.652	2000
2100	−4.987	−16.88	−5.701	−2.527	−3.419	−1.587	0.692	2100
2200	−4.477	−15.79	−5.125	−2.207	−3.094	−1.484	0.729	2200
2300	−4.012	−14.81	−4.600	−1.917	−2.797	−1.391	0.761	2300
2400	−3.585	−13.90	−4.118	−1.652	−2.525	−1.306	0.788	2400
2500	−3.192	−13.06	−3.675	−1.412	−2.274	−1.227	0.810	2500
2600	−2.830	−12.29	−3.266	−1.194	−2.043	−1.154	0.828	2600
2700	−2.495	−11.58	−2.887	−0.995	−1.829	−1.087	0.840	2700
2800	−2.183	−10.92	−2.536	−0.813	−1.631	−1.025	0.849	2800
2900	−1.893	−10.30	−2.208	−0.646	−1.446	−0.967	0.855	2900
3000	−1.622	−9.729	−1.903	−0.491	−1.273	−0.913	0.859	3000
3100	−1.369	−9.191	−1.617	−0.347	−1.111	−0.863	0.863	3100
3200	−1.131	−8.686	−1.349	−0.208	−0.960	−0.815	0.869	3200
3300	−0.908	−8.213	−1.097	−0.073	−0.818	−0.771	0.881	3300
3400	−0.698	−7.767	−0.860	0.062	−0.684	−0.729	0.900	3400
3500	−0.501	−7.346	−0.637	0.202	−0.558	−0.690	0.929	3500

Log(k)

4

Source: Pulkrabek

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)

$$C_\alpha H_\beta + \gamma(\alpha + \frac{\beta}{4})(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + dN_2 + eCO + fH_2$$
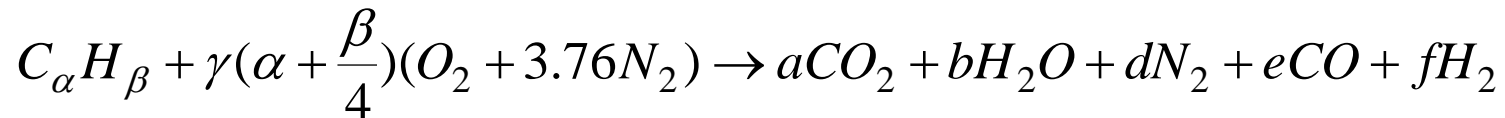
If the product species CO_2, H_2O, CO and H_2 are at equilibrium, an additional equation can be obtained from the water-gas reaction:

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

The equilibrium constant for this reaction provides the fifth equation:

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

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.

$$CO_2 + 1/2O_2 + 1/2N_2 \rightarrow \underbrace{aCO + bNO + cCO_2 + dO_2 + eN_2}$$

3000K and 1 atm
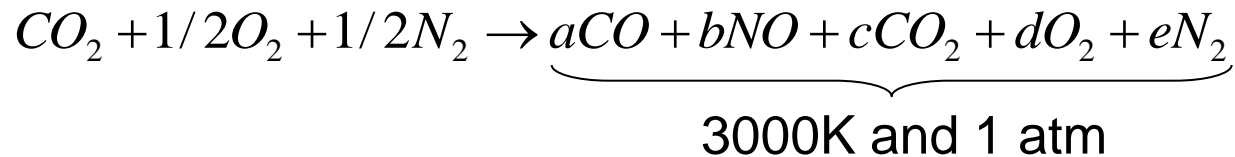
C	$1 = a + c$	$c = 1 - a$
O	$3 = a + b + 2c + 2d$	$d = 1/2(1 + a - b)$
N	$1 = b + 2e$	$e = 1/2(1 - b)$

Have 2 unknowns a, b so need 2 equilibrium equations

$$1. \quad CO_2 \leftrightarrow CO + 1/2O_2 \qquad K_1(3000K) = 0.3273$$

$$2. \quad 1/2O_2 + 1/2N_2 \leftrightarrow NO \qquad K_2(3000K) = 0.1222$$

Chemical Equilibrium, example

$$CO_2 \leftrightarrow CO + 1/2O_2$$

From the equilibrium constant expression

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

$$CO_2 + 1/2O_2 + 1/2N_2 \rightarrow aCO + bNO + cCO_2 + dO_2 + eN_2$$

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

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

Substituting yields:

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

Chemical Equilibrium, example

Similarly for the second equilibrium reaction

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

Solving equations 1 and 2 yields:

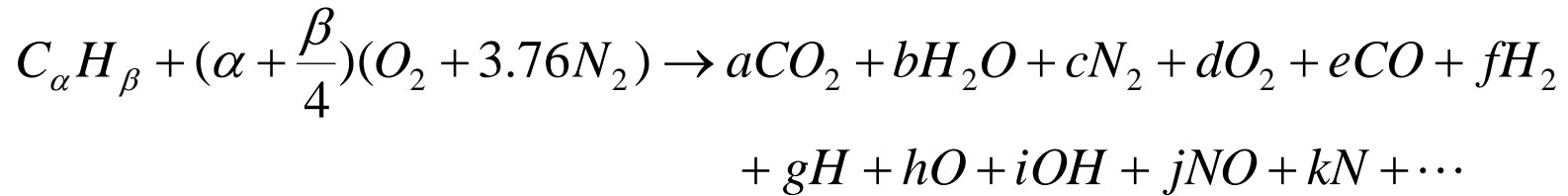$$a = 0.3745 \quad b = 0.0675$$

From the atom balance equations get:

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

Substituting and dividing through by the total number of moles gives:

$$0.17CO + 0.03NO + 0.29CO_2 + 0.30O_2 + 0.21N_2$$

Computer Programs 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 involved, one uses a computer program to calculate the product equilibrium composition.

http://www.wiley.com/college/mechs/ferguson356174/wave_s.html
        Equilibrium Combustion Solver Applet

A popular program used for chemical equilibrium calculations is STANJAN
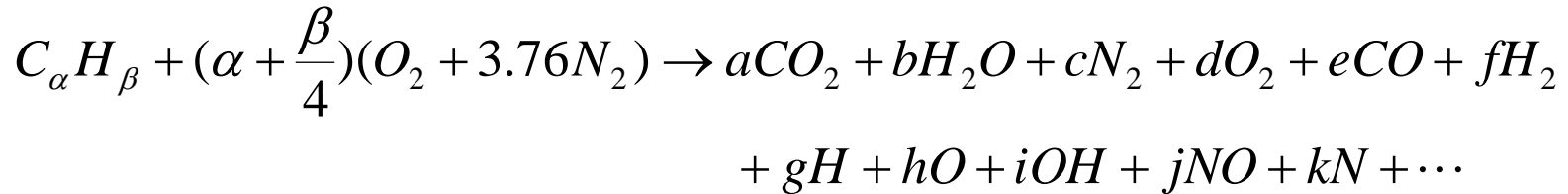
Equilibrium Composition for Combustion Products of Octane(C_8H_{18})-air
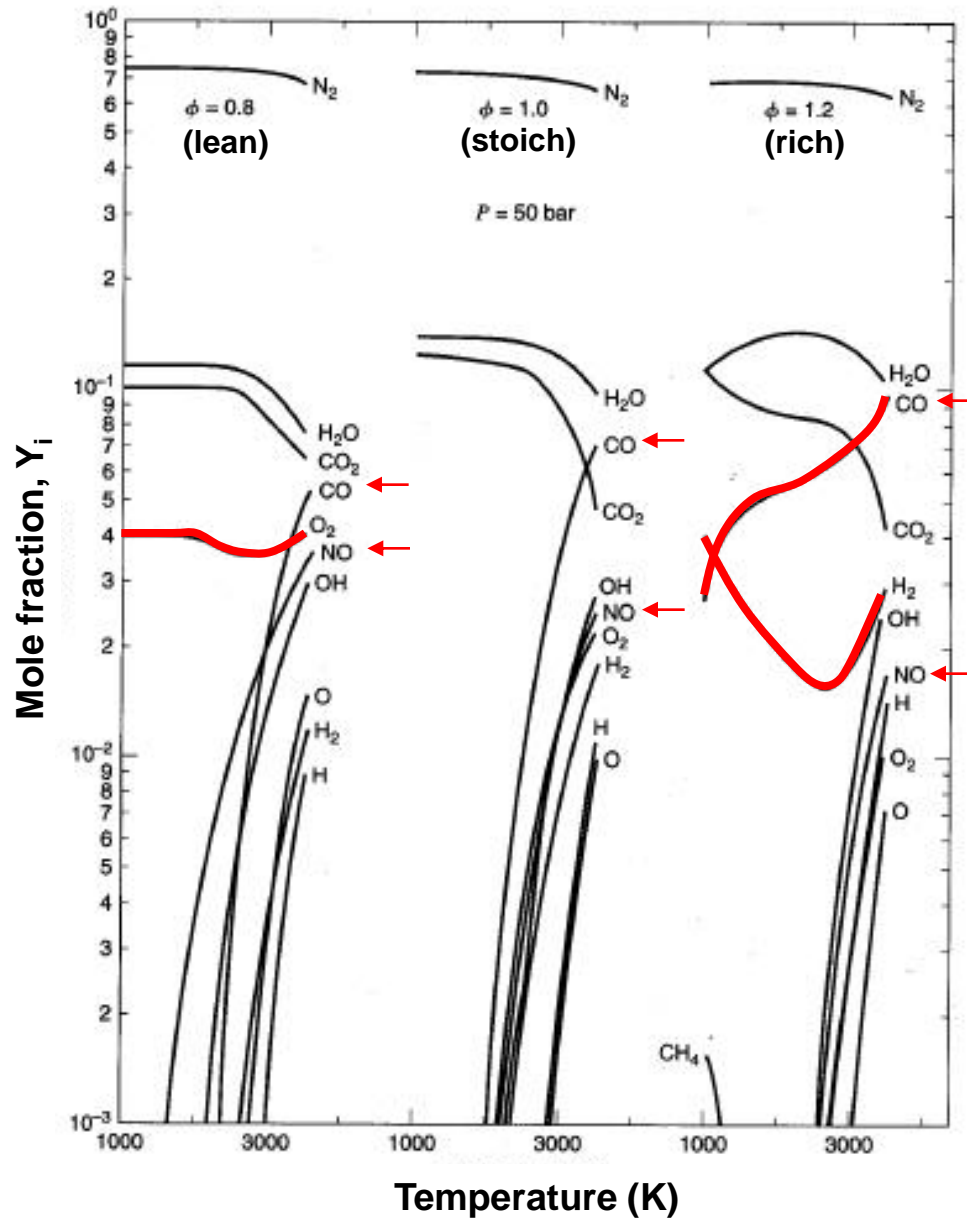
N_2, H_2O and CO_2 dissociate at high T

CH_4, NO and CO are air pollutants

Adiabatic Flame Temperature for Products at Equilibrium

$$C_\alpha H_\beta + (\alpha + \frac{\beta}{4})(O_2 + 3.76 N_2) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2 + eCO + fH_2$$

$$+ gH + hO + iOH + jNO + kN + \cdots$$

One can calculate the AFT for the above stoichiometric reaction where the products are at equilibrium: $\sum_P n_i \bar{h}_i(T_a) = \sum_R n_i \bar{h}_i(T_1)$

Dissociation of the products will result in a lower AFT since dissociation reactions are endothermic.
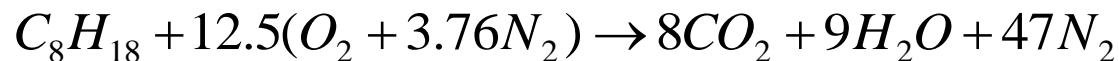
Again computer programs are used for these calculations:
http://www.wiley.com/college/mechs/ferguson356174/wave_s.html
Adiabatic Flame Temperature Applet

and STANJAN

Chemical Kinetics

Global (or overall) reactions describe the initial and final states:

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

First and Second Laws of thermodynamics are used to predict the final equilibrium state of the products after the reaction is complete.

Chemical kinetics deals with how fast the reaction proceeds.

$$v_F F + v_A A \rightarrow v_C C + v_D D$$
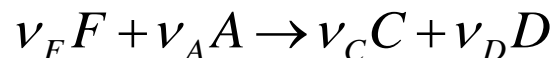
How fast the fuel is consumed is of interest, the **reaction rate** ω''' is defined as:
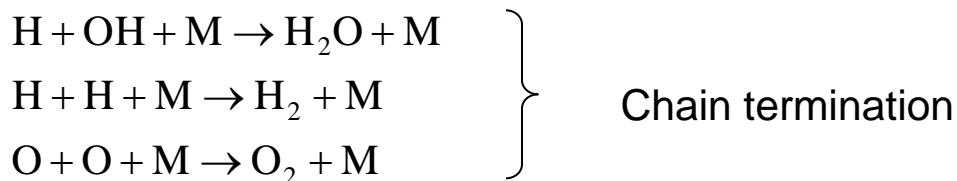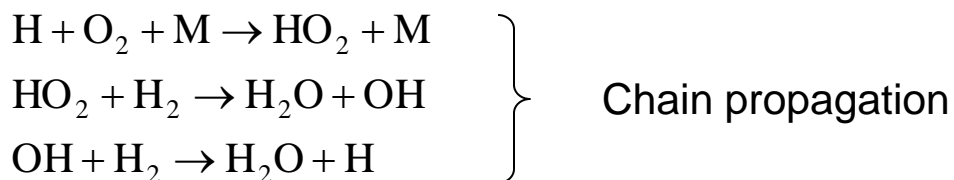
$$\omega''' = -\frac{d[F]}{dt} \qquad\qquad [F] = \frac{n}{V} = \frac{P_i}{\Re T}$$

where [F] refers to the fuel concentration ($kmol/m^3$ or kg/m^3), negative sign due to the fact that the fuel is consumed.

Reaction Mechanism

In reality the reaction proceeds through elementary reactions in a chain process known as chain reactions

The global hydrogen-oxygen reaction proceeds via the following subset of elementary reactions, collectively known as a **reaction mechanism**:

$$H_2 + M \rightarrow H + H + M \qquad \left.\right\}\; \text{Chain initiation}$$

$$\left.\begin{array}{l} H + O_2 + M \rightarrow HO_2 + M \\ HO_2 + H_2 \rightarrow H_2O + OH \\ OH + H_2 \rightarrow H_2O + H \end{array}\right\} \quad \text{Chain propagation}$$

$$\left.\begin{array}{l} H + O_2 \rightarrow OH + O \\ H_2 + O \rightarrow OH + H \end{array}\right\} \quad \text{Chain branching}$$

$$\left.\begin{array}{l} H + OH + M \rightarrow H_2O + M \\ H + H + M \rightarrow H_2 + M \\ O + O + M \rightarrow O_2 + M \end{array}\right\} \quad \text{Chain termination}$$

(*M* is any species present th at acts as a collision partner)

Chain Branching

In chain initiation reactions radicals are formed

In chain propagation reactions there is no net production or destruction of free radicals

In chain branching reactions there is a net production of radicals

Chain branching reactions lead to rapid production of radicals which causes the overall reaction to proceed extremely fast → explosively

The reaction comes to completion through chain termination reactions where the radicals recombine to form the final products.

Global Reaction Rate

Even for the simplest hydrocarbon fuels the chemistry is very complicated. The GRI HC mechanism has 49 species and 227 elementary reactions.

For engineering purposes easier to use approximate global reaction:

$$v_f \left(Fuel\right) + v_{O_2} O_2 + v_i \left(Inert\right) \rightarrow v_P \left(\text{Pr} \, oduct\right)$$
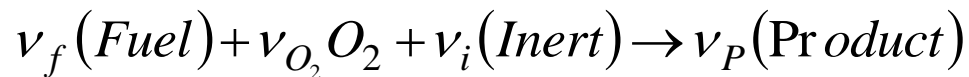
Empirical correlations have been developed for the fuel reaction rate:

$$\frac{d[Fuel]}{dt} = -A \exp\left(-\frac{E}{\bar{R}T}\right) \cdot [Fuel]^n [O_2]^m [Inert]^l$$

where   [ ] in units of gmol/cm^3
   $\bar{\bar{R}}$ = 1.987 cal/gmolK
   E typically 20 - 40 kcal/gmol

Note typically l= 0