Ciências
ULisboa

Faculdade
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da Universidade
de Lisboa

DISCIPLINA LEEA

Technologies of combustion

Corpo docente

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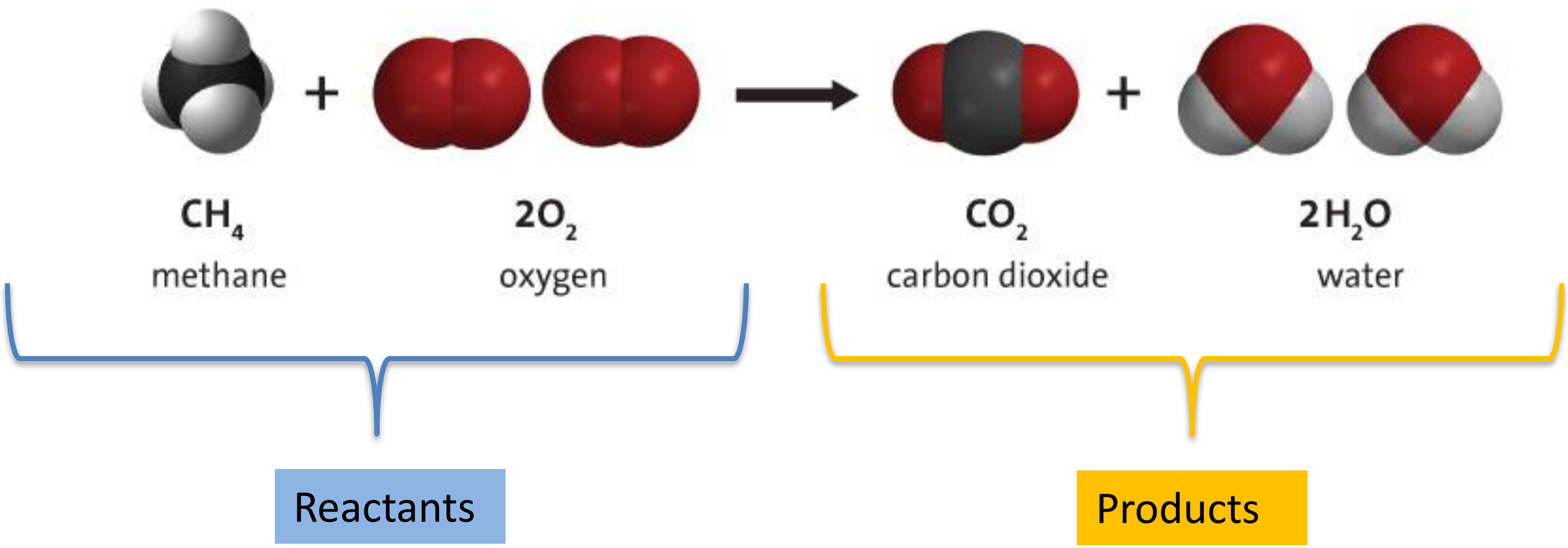
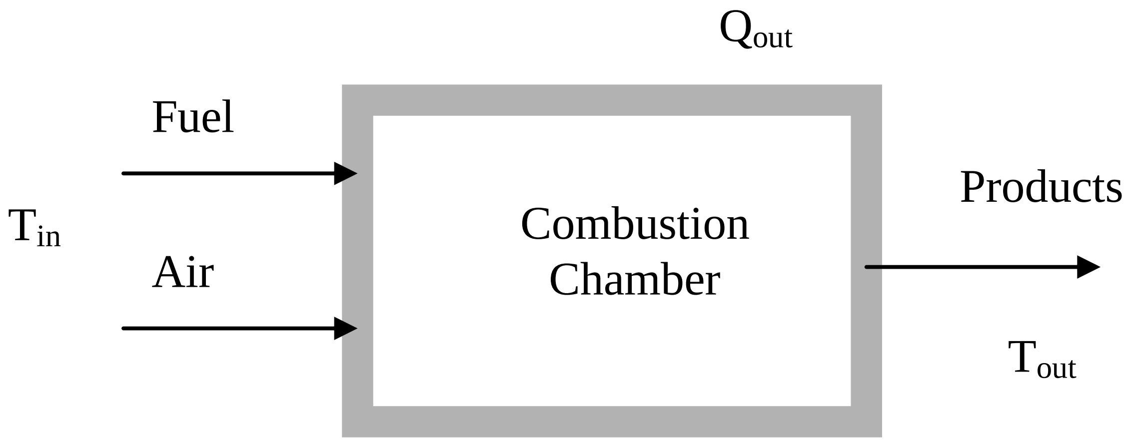
Thermochemistry



Thermochemistry



- Maximum heat release, max Q_{out}: T_{out}=T_{in}
- Maximum flame temperature, T_{ad}:

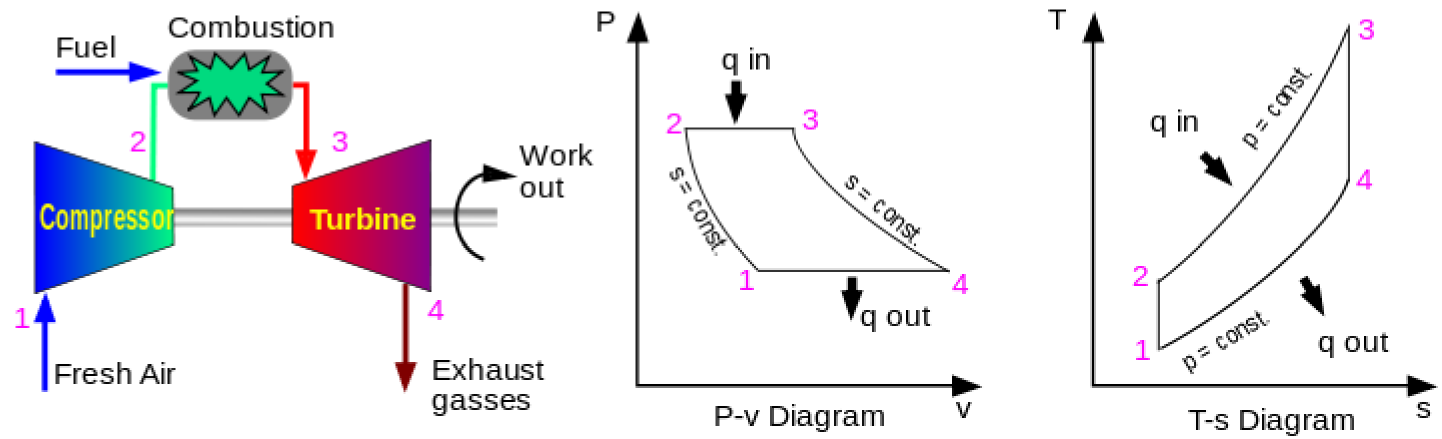
Hreag(T_{in})=Hprod (T_{ad})(constant pressure, e.g. Diesel engine, gas turbine, furnace)

Hreag(T_{in})=Hprod (T_{ad})-R($n_{prod}T_{ad}$-$n_{reag}T_{in}$) (constant volume, e.g. gasoline engine)

Thermochemistry

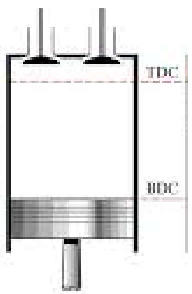
Hreag(T_{in})=Hprod (T_{ad}) (constant pressure, e.g. Diesel engine, **gas turbine**, furnace)

Brayton cycle



Thermochemistry

$Hreag(T_{in})=Hprod\ (T_{ad})-R(n_{prod}T_{ad}-n_{reag}T_{in})$ (constant volume, e.g. **gasoline engine**)



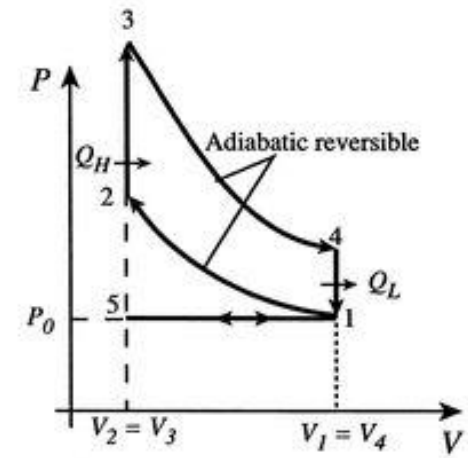
Top Dead Centre

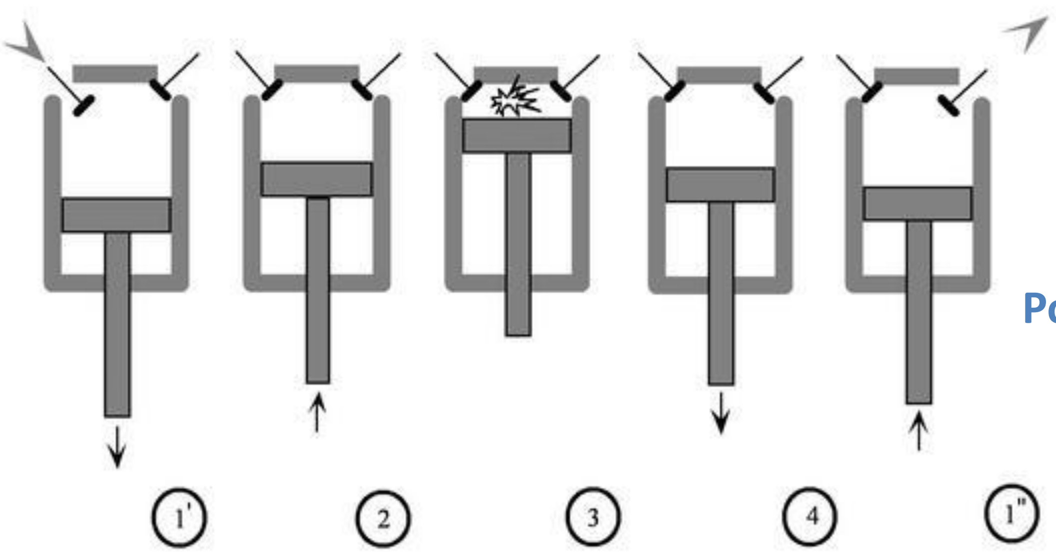
- ***Ponto morto superior***

Bottom Dead Centre

- ***Ponto morto inferior***

Otto cycle

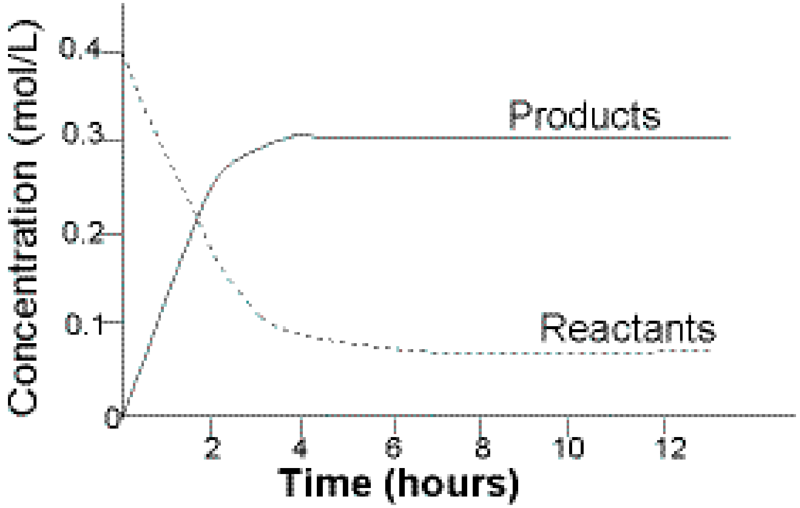




Ponto morto superior

Ponto morto inferior

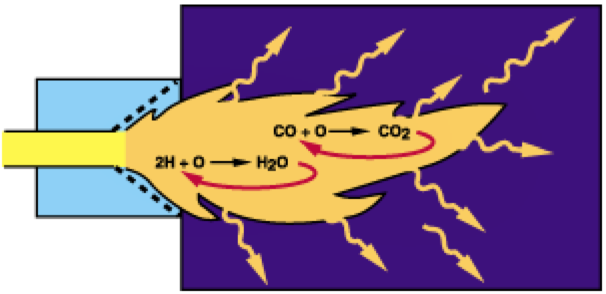
Chemical equilibrium



Chemical equilibrium is the state reached when the concentrations of the products and reactants **remain constant over time**. The mixture of reactants and products in the equilibrium state is the **equilibrium mixture**.

Thermochemistry

Usually temperatures are higher than 1250 K……other species form trough **dissociation reactions**



Chemical Reactions

$$H_2O \rightarrow H_2 + 1/2 O_2 \quad (1)$$

$$H_2 \rightarrow 2H \quad (2)$$

$$O_2 \rightarrow 2O \quad (3)$$

$$O + H \rightarrow OH \quad (4)$$

$$O + N_2 \leftrightarrow N + NO$$
$$O_2 + N \leftrightarrow O + NO$$
$$N + OH \rightarrow H + NO$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$2\ CO(g) + O_2(g) \rightleftharpoons 2\ CO_2(g)$$

$$H_2 \leftrightarrow 2H$$
$$O_2 \leftrightarrow 2O$$
$$N_2 \leftrightarrow 2N$$
$$O_2 + H_2 \leftrightarrow 2OH$$
$$CO + O_2 \leftrightarrow CO_2 + O$$
$$H_2O + O \leftrightarrow 2OH$$

Chemical Equilibrium

- In general the combustion products consist of more than just CO_2, H_2O 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:

$CO + H_2O \Leftrightarrow CO_2 + H_2$

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

- 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 and 2nd law thermodynamics

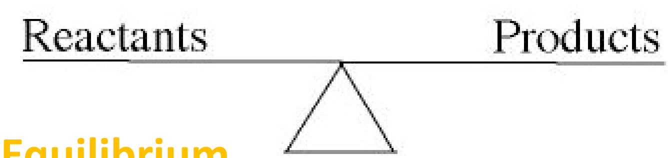
$$\Delta S = \oint \frac{\partial Q}{T} + \sigma$$

σ >=0 entropy generation

T=control volume temperature

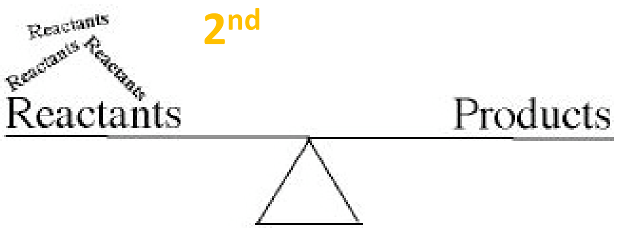
G=H-TS Free Gibs Energy

Le chatelier

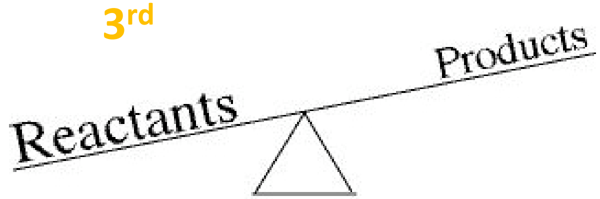


1st Equilibrium

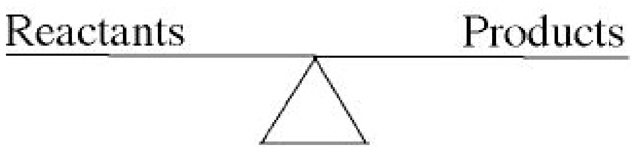
2nd



3rd



4th Equilibrium again



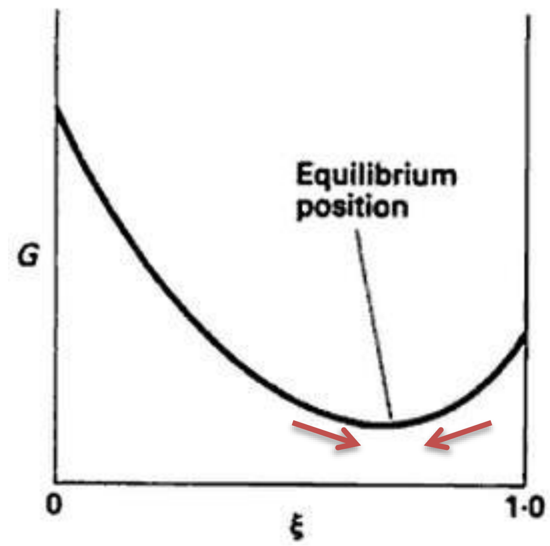
Chemical Equilibrium

G=H-TS Free Gibs Energy

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

@equilibrium,dG=0

$$K = exp\left[-\frac{\Delta G^0(T)}{RT}\right] = \frac{p_C{}^{nC} . p_D{}^{nD}}{p_A{}^{nA} . p_B{}^{nB}}$$



Le chatelier

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 forward (f) reaction for species A, B TO TRANSFORM IN C, D and REVERSE (r) ratio is given by:

Kp

$$\frac{kf}{kr} = exp\left[-\frac{\Delta G^0(T)}{RT}\right] = \frac{p_C{}^{nC} . p_D{}^{nD}}{p_A{}^{nA} . p_B{}^{nB}}$$

Chemical Equilibrium

K is the **equilibrium constant**

Kc

$$kf(T)/kr(T)=\frac{X_C^{n_C}\cdot X_D^{n_D}}{X_A^{n_A}\cdot X_B^{n_B}}$$

Forward reaction

Reverse reaction

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

Chemical Equilibrium

K is the **equilibrium constant**

$$Kp=Kc*\left(\frac{RT}{P_{ref}}\right)^{nprod-nreag}$$

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

Forward reaction

Reverse reaction

$$Note \quad X_A=\frac{n_A}{n_A+n_B+n_C+n_D}*p/RT=concentration$$

mol/m3

Chemical Equilibrium

K is the **equilibrium constant**

Kn

$$kf(T)/kr(T) = Kn(T) = \frac{n_C^{n_C} \cdot n_D^{n_D}}{n_A^{n_A} \cdot n_B^{n_B}}$$

Forward reaction

Reverse reaction

$$K_p = K_c * \left(\frac{RT}{P_{ref}}\right)^{n_{prod}-n_{reag}} = K_n * \left(\frac{P}{n_{Total}P_{ref}}\right)^{n_{prod}-n_{reag}}$$

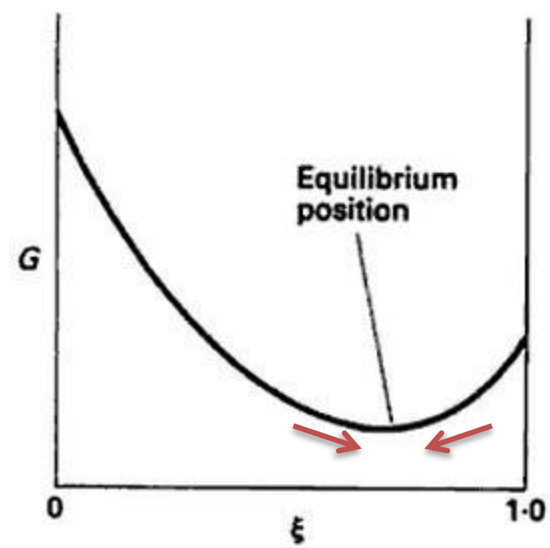
Chemical Equilibrium

K is the **equilibrium constant**

$$K_p = K_c * \left(\frac{RT}{P_{ref}}\right)^{n_{prod}-n_{reag}} = K_n * \left(\frac{P}{n_{Total}P_{ref}}\right)^{n_{prod}-n_{reag}}$$

P em bar

G=H-TS Free Gibs Energy



@equilibrium,dG=0

$$K = exp\left[-\frac{\Delta G^0(T)}{RT}\right] = \frac{p_A{}^{nA}.p_B{}^{nB}}{p_C{}^{nC}.p_D{}^{nD}}$$

Le chatelier

Chemical Equilibrium

K is tabulated as a function of temperature for different equilibrium reactions

APÊNDICE 4
CONSTANTES DE EQUILÍBRIO

$H_2+1/2O_2 \Leftrightarrow H_2O$ | $CO+1/2O_2 \Leftrightarrow CO_2$ | $CO_2+H_2 \Leftrightarrow CO+H_2O$ | $OH+1/2H_2 \Leftrightarrow H_2O$ | $1/2O_2+1/2N_2 \Leftrightarrow NO$ | $2H \Leftrightarrow H_2$ | $2O \Leftrightarrow O_2$ | $2N \Leftrightarrow N_2$

T (K)	$\log_{10} K_p$ com as pressões parciais em atmosferas							
	$\frac{p_{H_2O}}{p_{H_2}\sqrt{p_{O_2}}}$	$\frac{p_{CO_2}}{p_{CO}\sqrt{p_{O_2}}}$	$\frac{(p_{H_2O})(p_{CO})}{(p_{H_2})(p_{CO_2})}$	$\frac{p_{H_2O}}{p_{OH}\sqrt{p_{H_2}}}$	$\frac{p_{NO}}{\sqrt{p_{O_2}}\sqrt{p_{N_2}}}$	$\frac{p_{H_2}}{(p_H)^2}$	$\frac{p_{O_2}}{(p_O)^2}$	$\frac{p_{N_2}}{(p_N)^2}$
298	40,048	45,066	−5,018	46,181	−15,171	71,232	81,202	159,600
300	39,786	44,760	−4,974	45,876	−15,073	70,762	80,664	158,578
400	29,240	32,431	−3,191	33,600	−11,142	51,758	58,944	117,408
600	18,633	20,087	−1,454	21,264	−7,210	32,676	37,146	76,162
800	13,289	13,916	−0,627	15,060	−5,243	23,082	26,202	55,488
1000	10,062	10,221	−0,159	11,322	−4,062	17,294	19,612	43,056
1200	7,899	7,764	0,135	8,822	−3,275	13,416	15,208	34,754
1400	6,347	6,014	0,333	7,030	−2,712	10,632	12,054	28,812
1600	5,180	4,706	0,474	5,686	−2,290	8,534	9,684	24,350
1800	4,270	3,693	0,577	4,638	−1,962	6,896	7,836	20,874
2000	3,540	2,884	0,656	3,799	−1,699	5,582	6,356	18,092
2200	2,942	2,226	0,716	3,113	−1,484	4,504	5,142	15,810
2400	2,443	1,679	0,764	2,541	−1,305	3,602	4,130	13,908

Tabela A4.1
Constantes de equilíbrio. (Dados extraídos de Rogers e Mayhew, 1994.) (continua)

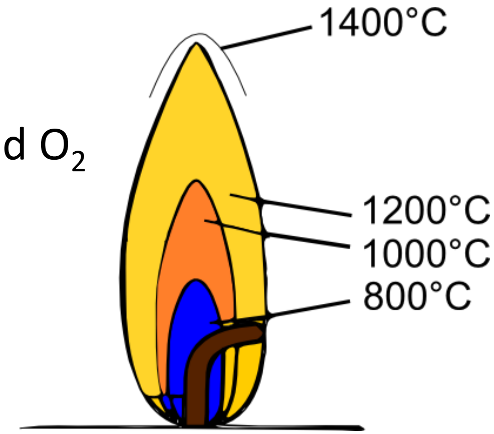
Thermochemistry

Chemical equilibrium

T< 1250 K

λ>=1 (stoichiometric/poor)

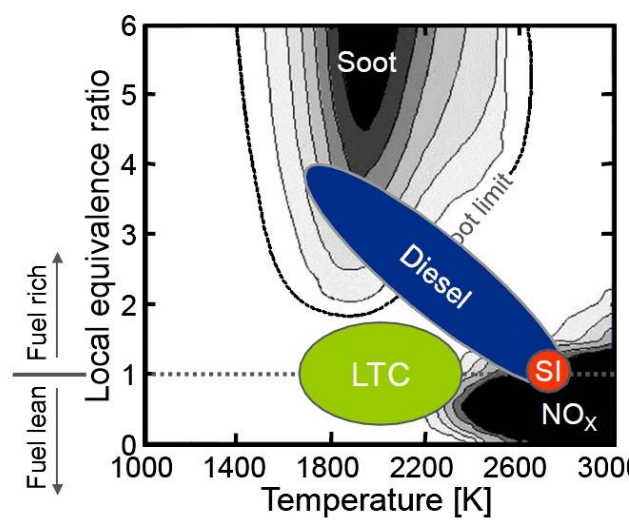
$\Rightarrow$ Complete combustion
Stable chemical species: CO_2, H_2O, N_2 and O_2



Usually temperatures are higher than 1250 K……e.g.

Spark plug

Injector

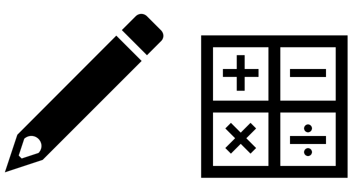


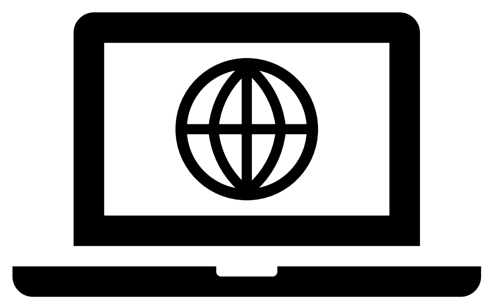
Role of Equilibrium Solvers

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

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

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





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Equilibrium Solvers

TITLE AND SUBTITLE:

Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications II. User's Manual and Program Description

AUTHOR(S):

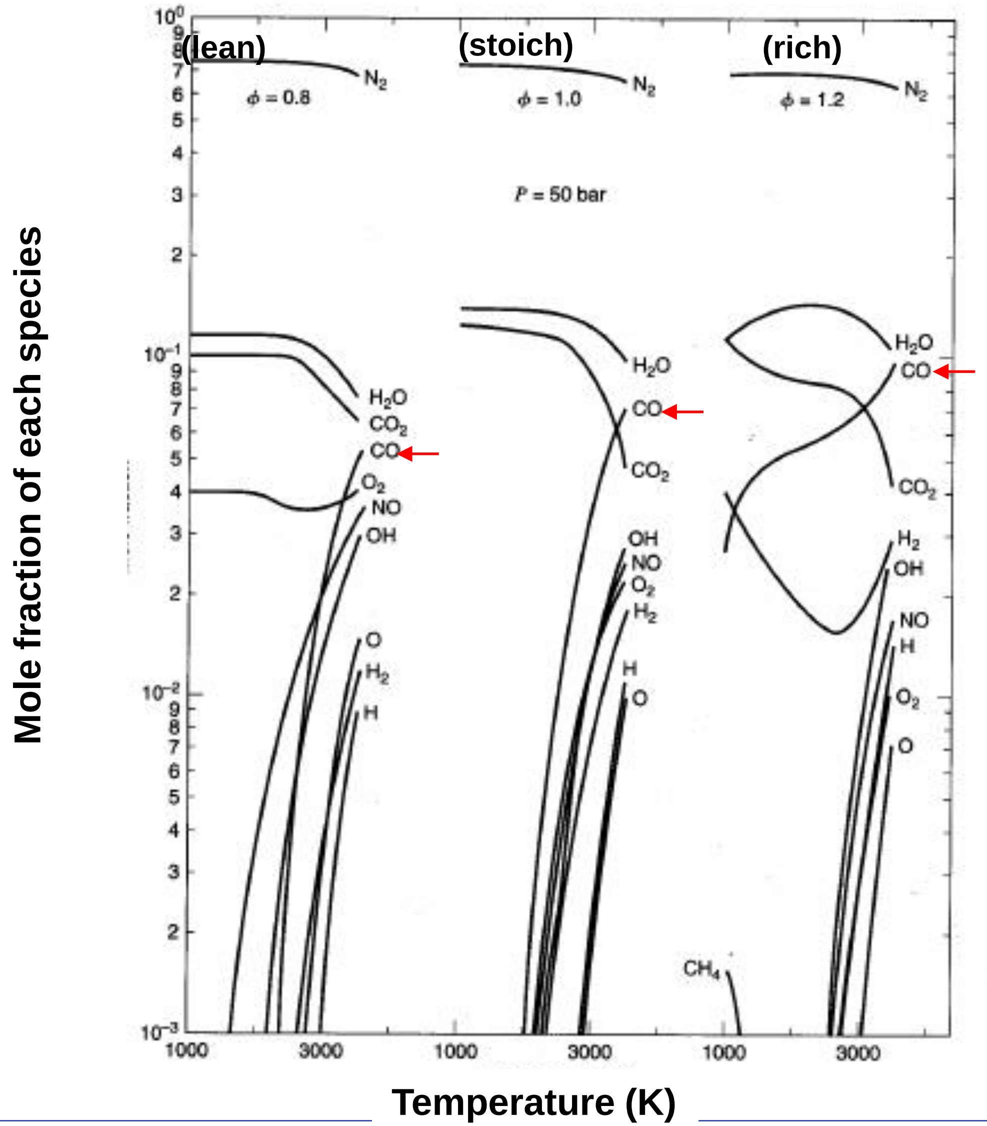
Bonnie J. McBride and Sanford Gordon

REPORT DATE:

June 1996

Composition of Octane-air Mixtures at Equilibrium

C8H18



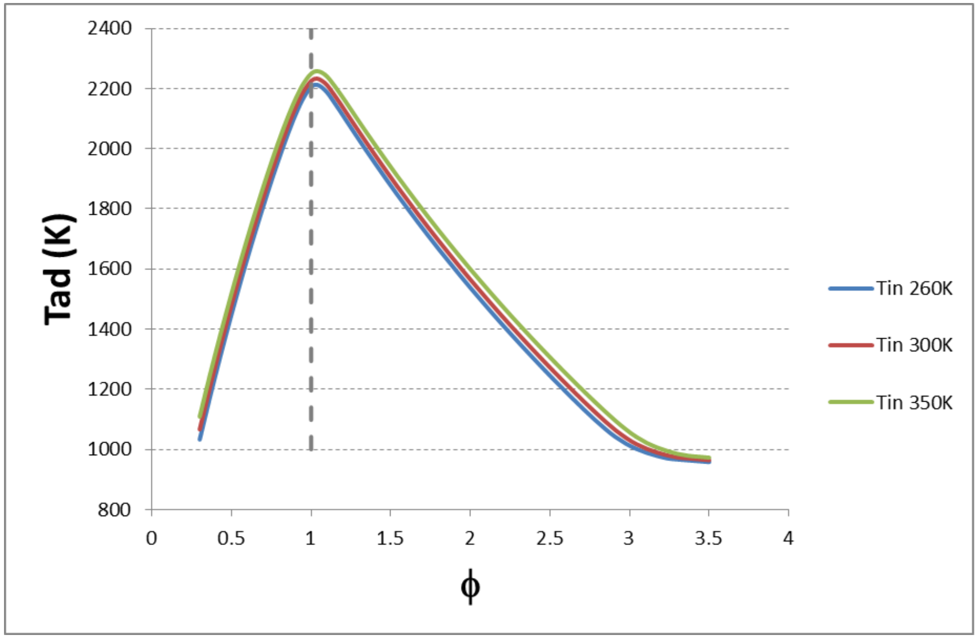
Cantera

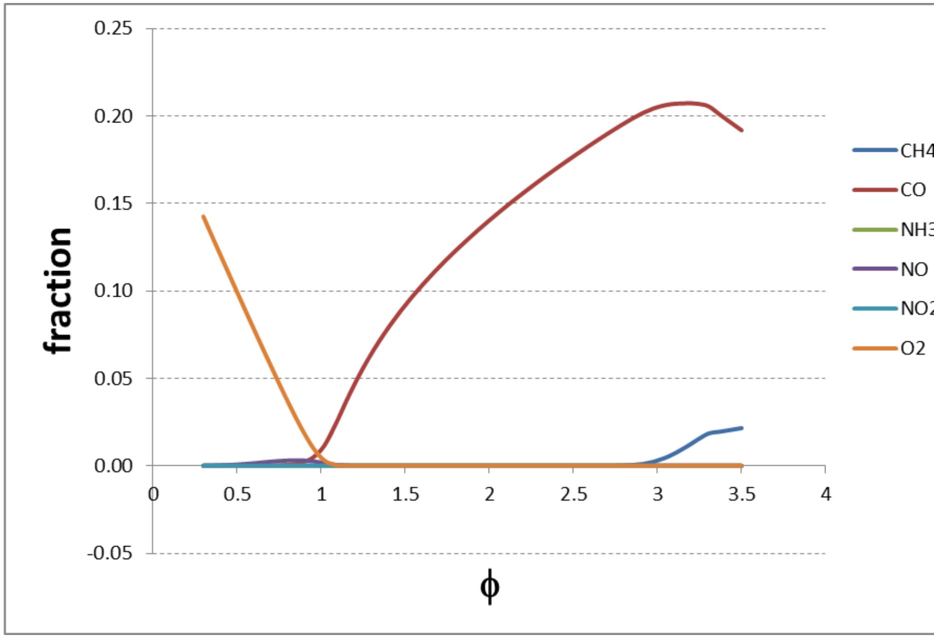
Cantera
Chemical Kinetics • Thermodynamics • Transport Processes

CONDA

http://www.cantera.org/docs/sphinx/html/cython/examples/multiphase_adiabatic.html

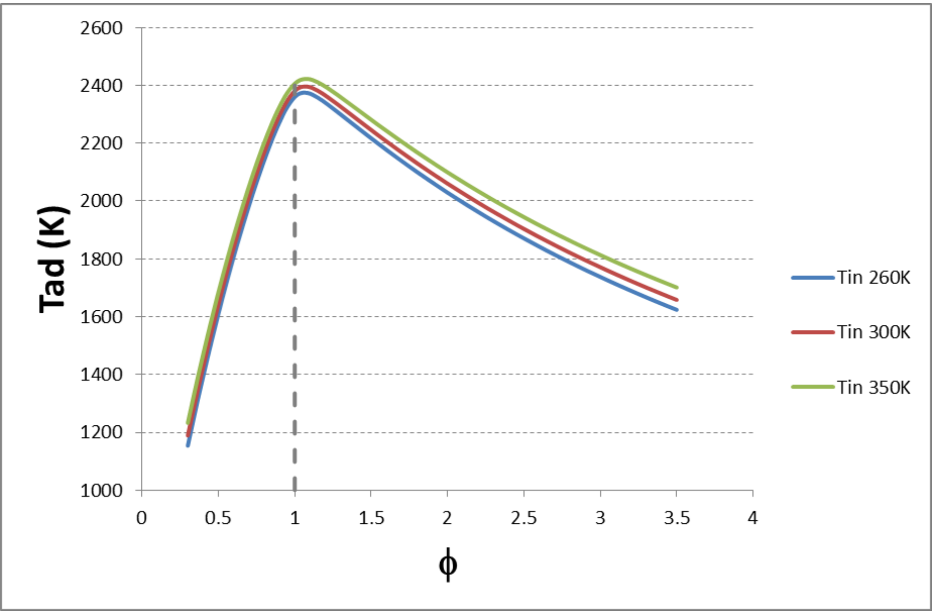
Cantera CH4

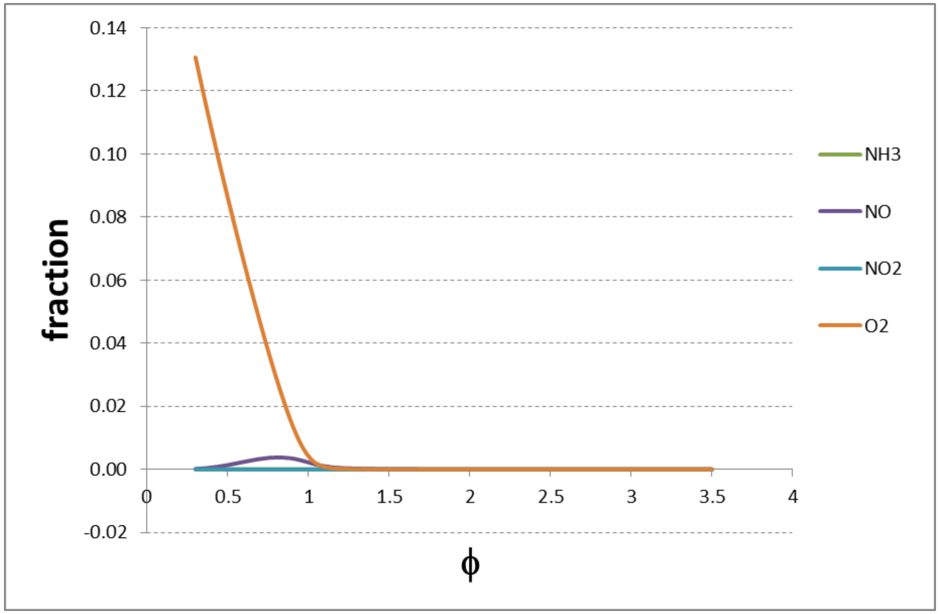




http://www.cantera.org/docs/sphinx/html/cython/examples/multiphase_adiabatic.html

Cantera H2





http://www.cantera.org/docs/sphinx/html/cython/examples/multiphase_adiabatic.html

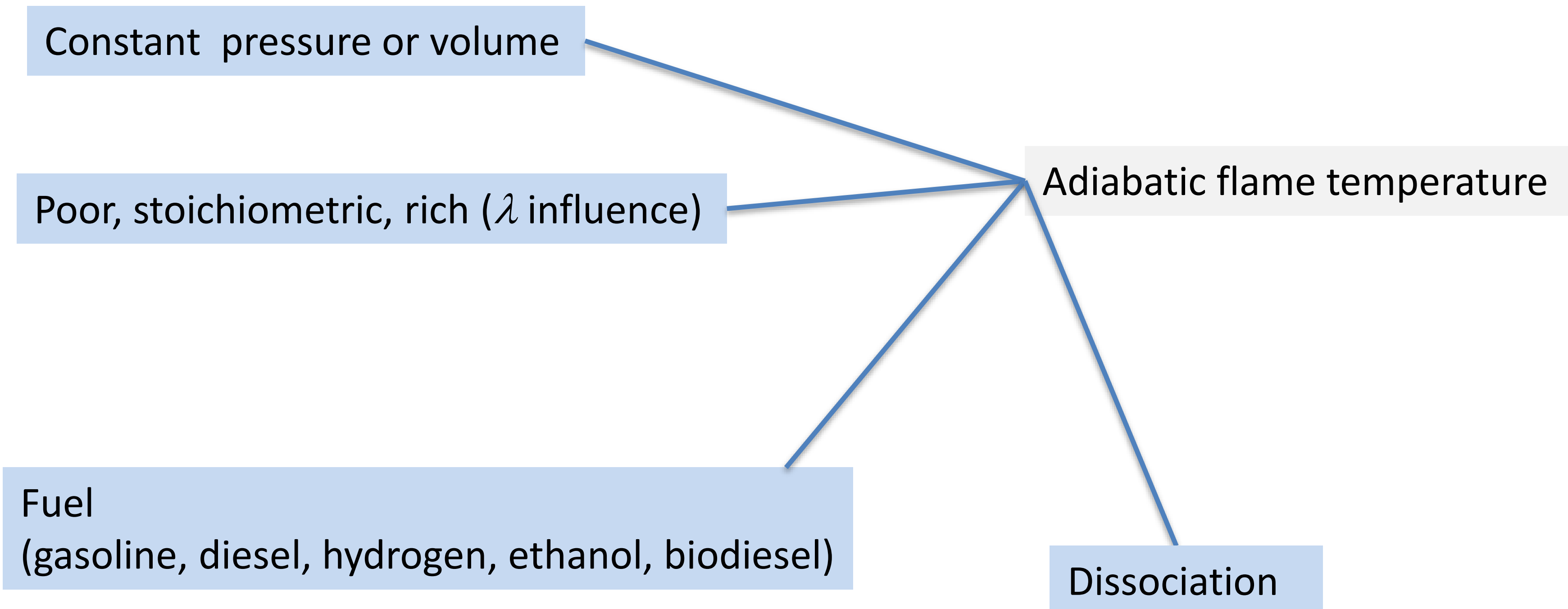
Chemical Equilibrium

P#8 Consider the stoichiometric combustion of methane (CH_4) at standard conditions with dissociation. Assume the following species in equilibrium CO_2, H_2O, O_2, CO, H_2 e N_2

a) Compute the chemical equilibrium concentrations at 2000 K.

b) Compute the adiabatic flame temperature and compare with the adiabatic flame temperature without dissociation.

Adiabatic Temperature



Adiabatic???

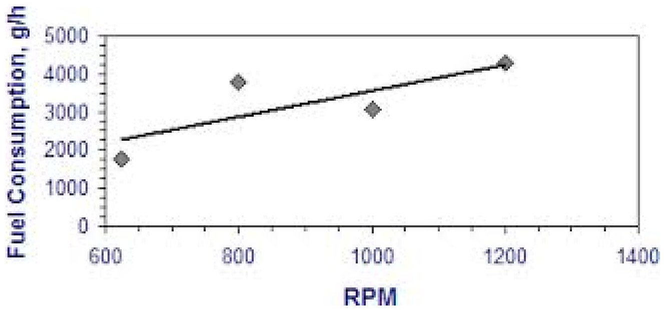
Combustion reactions generally occur very fast ~ 1ms

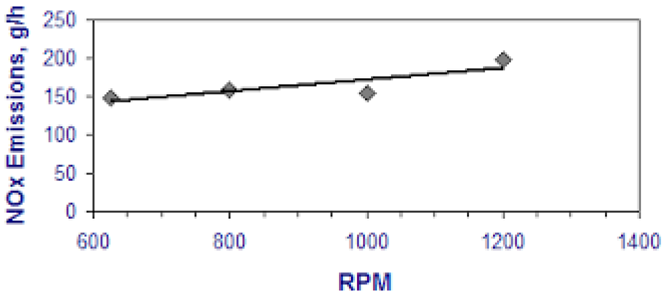
↓

Little heat or work transfer takes place

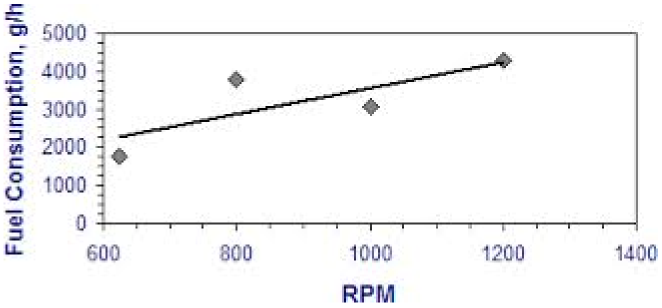
↓

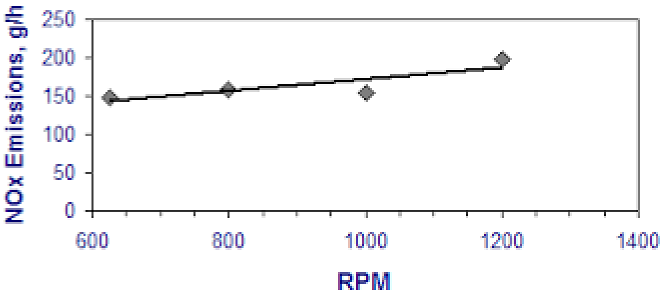
Maximum temperature achieved is often near Tad

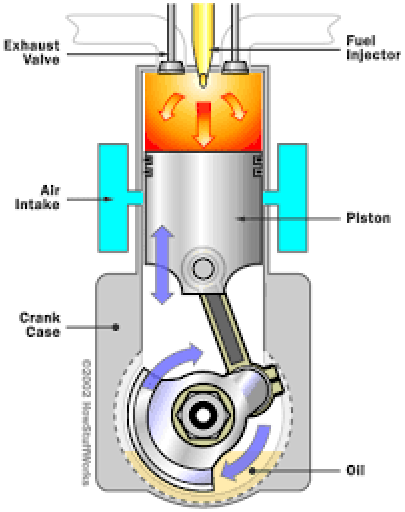




Adiabatic???





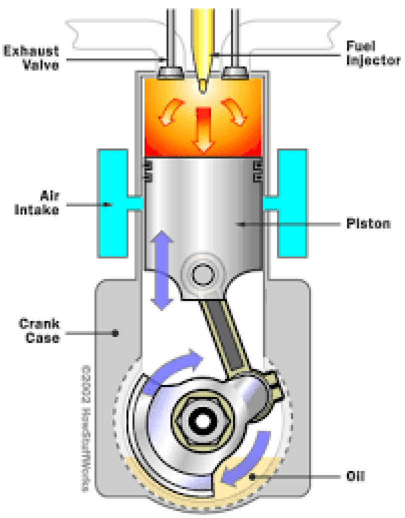


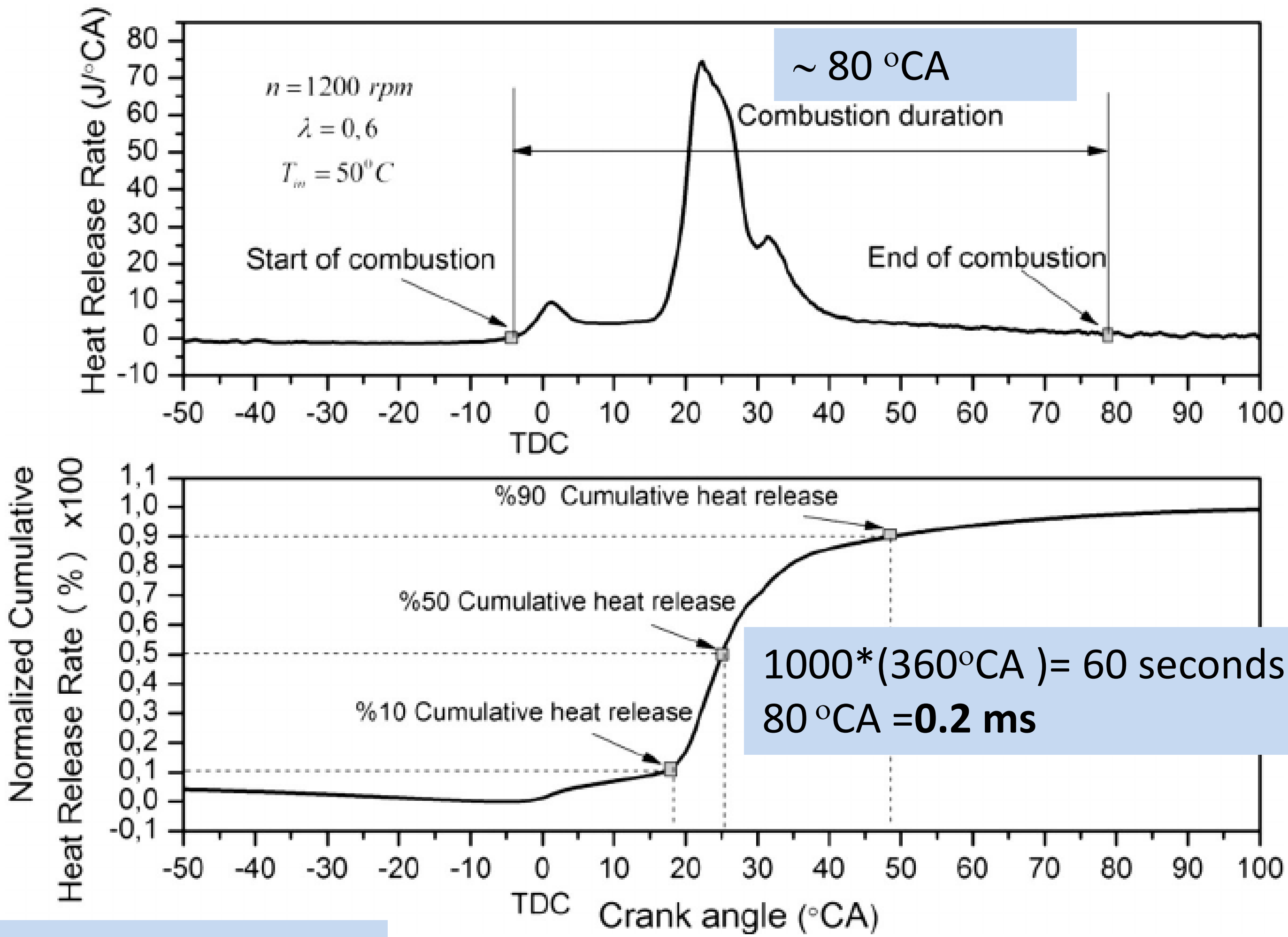
1000 rpm= 1000 revolutions per minute

1 revolution is 360ºCA (Crank angle)

1000*(360ºCA)= 60 seconds

Adiabatic???





~ 80 ºCA

1000*(360ºCA)= 60 seconds

80 ºCA =**0.2 ms**

More rpm, less combustion time!!!

NOx formation

NO_X means the sum of NO and NO_2 contents in flue gas recalculated on NO_2
NO x = NO + NO_2 (expressed in NO_2)

$$NO_x \text{ [ppm]} = NO \text{ [ppm]} + NO_2 \text{ [ppm]}$$

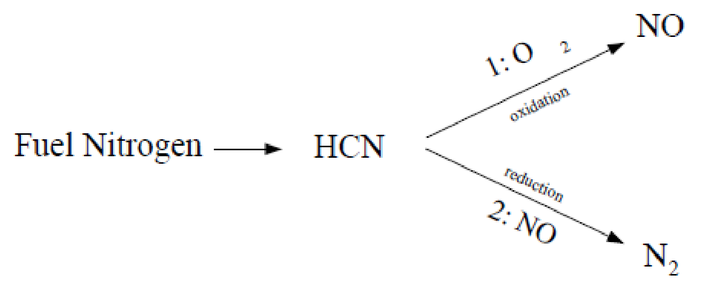
The NOx content in the combustion gases from conventional power plant boilers and many industrial heating process contains some **90 % NO** with the remainder NO_2

- **THERMAL NITRIC OXIDE MECHANISM is usually the most important**
- **Fuel NOx**
- **Prompt NOx**

NOx formation

- **Prompt NOx**
- **Fuel NOx**
- **THERMAL NITRIC OXIDE MECHANISM is usually the most important**

Prompt NOx: Formed in the flame zone through intermediate formation of hydrogen cyanide (HCN) followed by a subsequent oxidation of HCN to NO



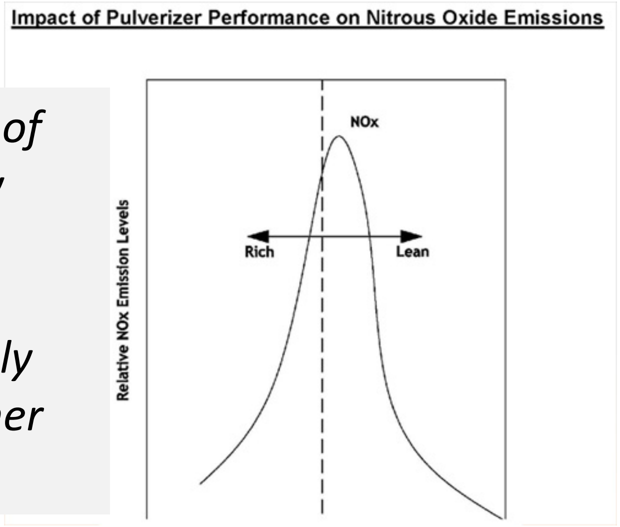
NOx formation

Fuel NOx: Nitrogen accounts for about 1.5 wt% of most coals.

	<---------- Low	Rank -------><----	High	Rank ------------>
Rank:	Lignite	Subbituminous	Bituminous	Anthracite
Age:	------------------------------------	increases	------------------------------------	
% Carbon:	65-72	72-76	76-90	90-95
% Hydrogen:	~5 ----------------------	decreases	---------------------- ~2	
% Nitrogen:	<----------------------------------	~1-2	---------------------------------->	
% Oxygen:	~30 ----------------------	decreases	---------------------- ~1	
% Sulfur:	~0 -----------	increases -----------	~4 --- decreases	--- ~0
%Water:	70-30	30-10	10-5	~5
Heating value (BTU/lb):	~7000	~10,000	12,000–15,000	~15,000

FIGURE 7-3. Variation of selected coal properties with coal rank.

The conversion of fuel N is weakly temperature dependent but depends strongly upon local burner stoichiometry.



@http://www.ems.psu.edu/~radovic/Chapter7.pdf

NOx formation

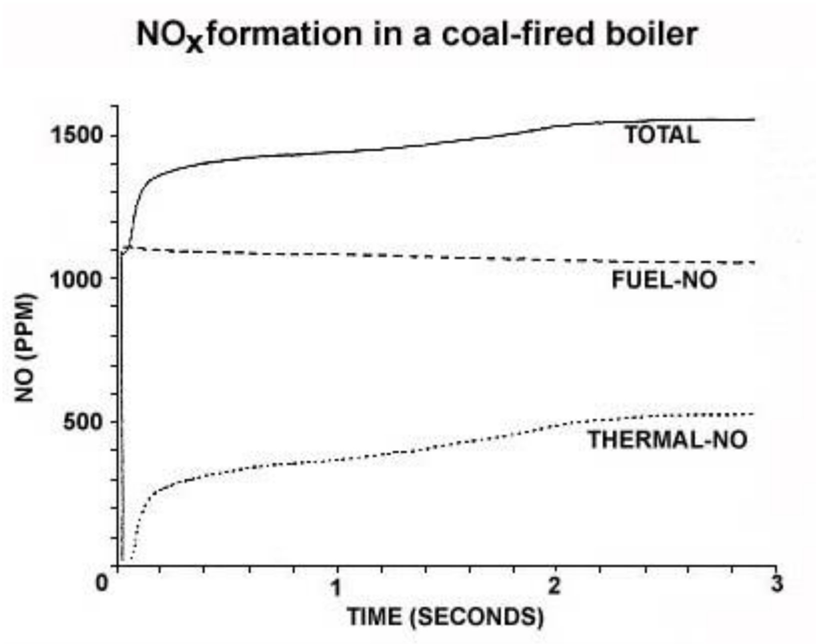
Thermal NOx: The three principal reactions (the extended **Zeldovich mechanism**) producing thermal NO_x are:

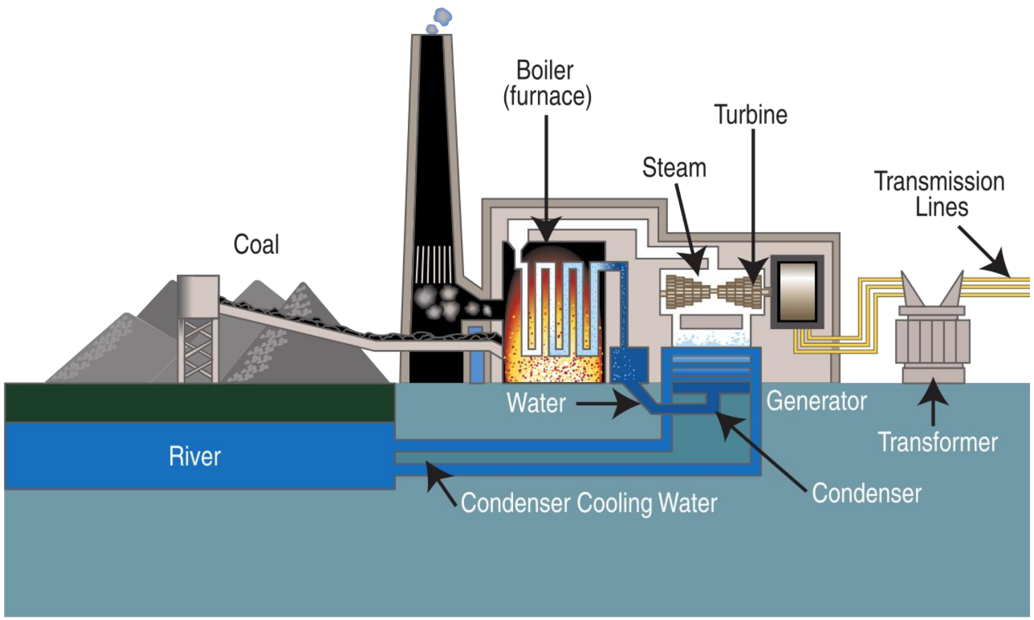
$N_2 + O \rightarrow NO + N$

$N + O_2 \rightarrow NO + O$

$N + OH \rightarrow NO + H$

NOx emisisons





ppm ☺ !!!!

EGR influence Emissions

Exhaust gas recirculation and aftertreatment (lean combustion)

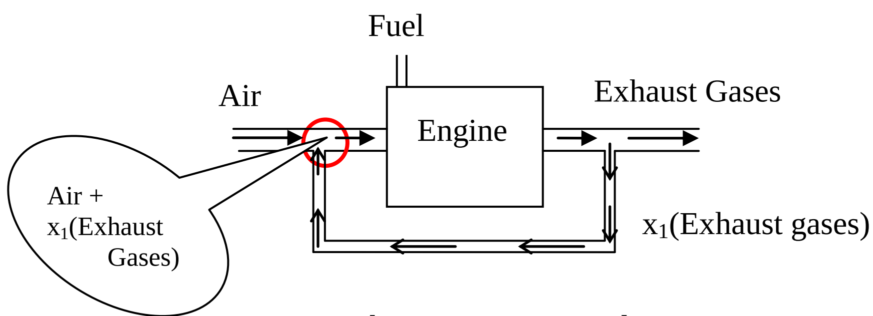
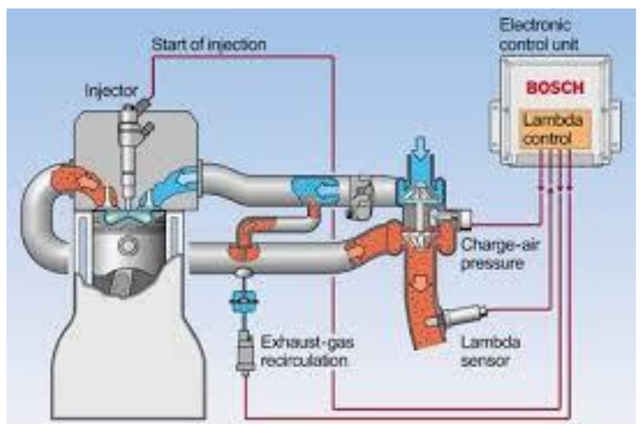
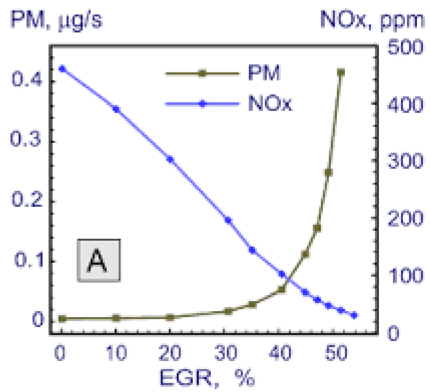


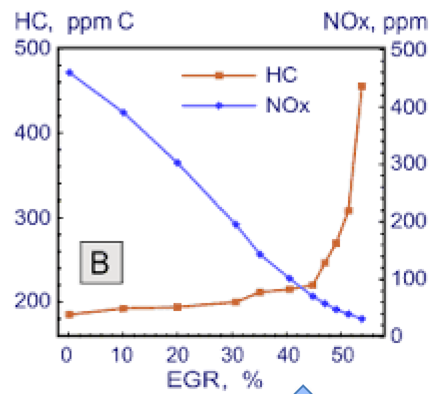
Figure 2: Exhaust Gas Re- circulation

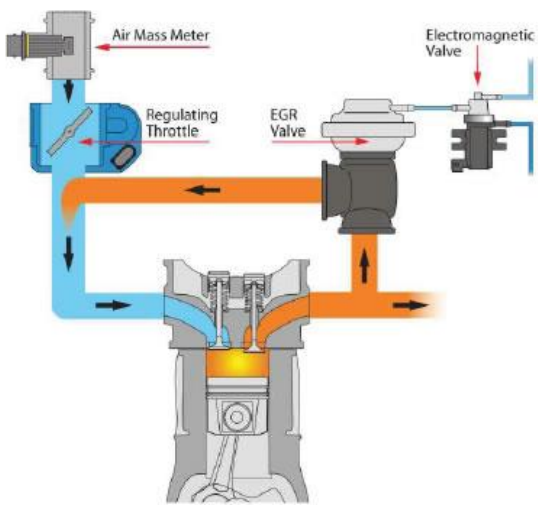


EGR influence Emissions

Exhaust gas recirculation and aftertreatment







Objective: minimize emissions

Optimum EGR……trade-offs
typically less than 30%

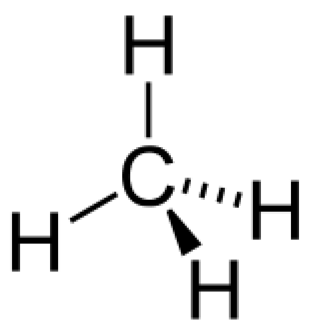
HC Emissions

Unburned hydrocarbons included in → **VOC**

→ **NMVOC (non-methane volatile organic compounds) pollutant**

→ **MVOC (methane volatile organic compounds) greenhouse gas**

Organic compounds are a class of complex molecules that are characterized by their use of carbon as a molecular backbone

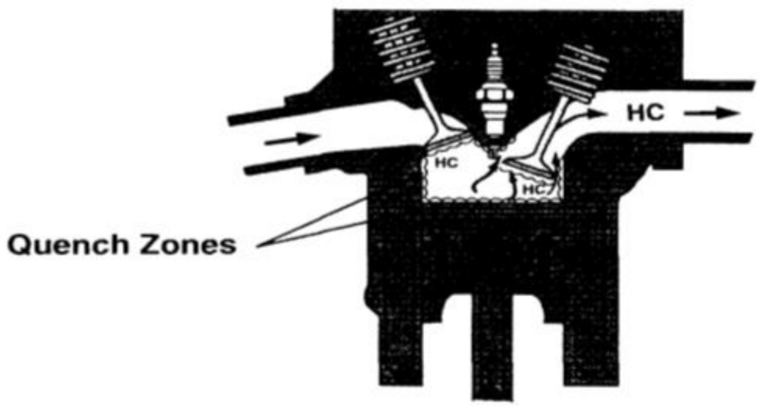


HC Emissions

Unburned hydrocarbons

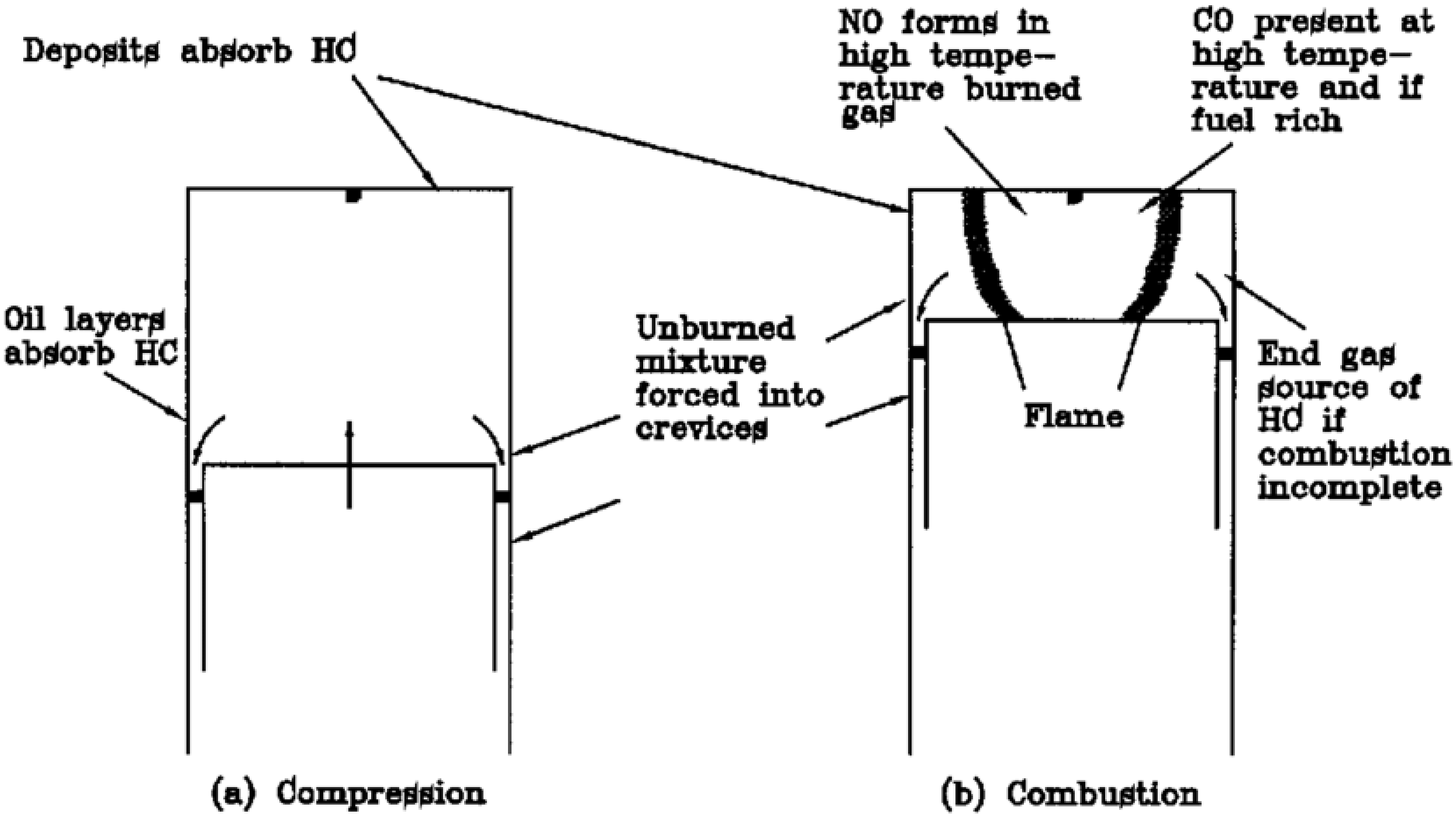
"Quenching"

Quenching occurs when the combustion flame-front is extinguished before all the fuel is burned.

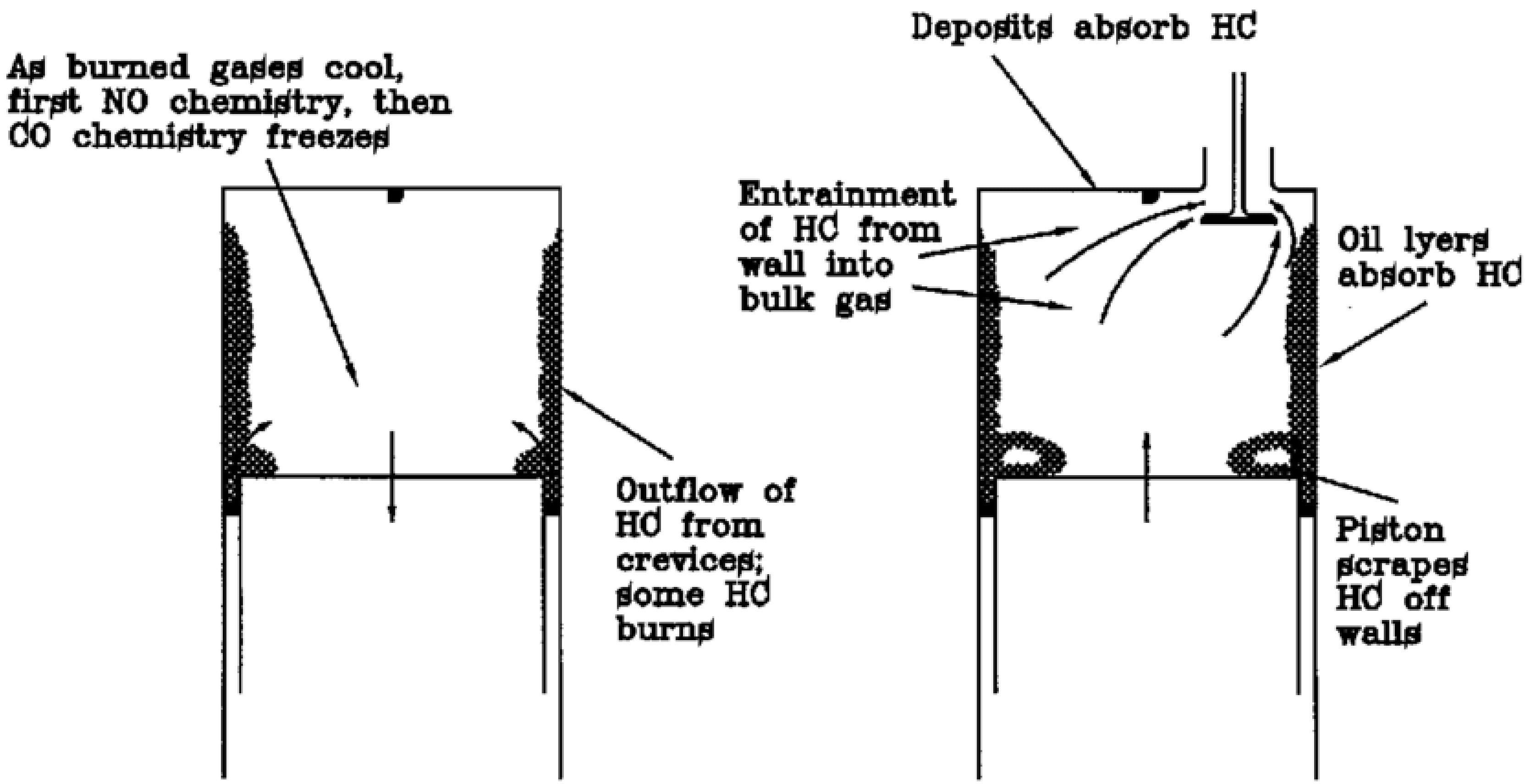


Wall quenching

HC Emissions



HC Emissions



(c) Expansion (d) Exhaust

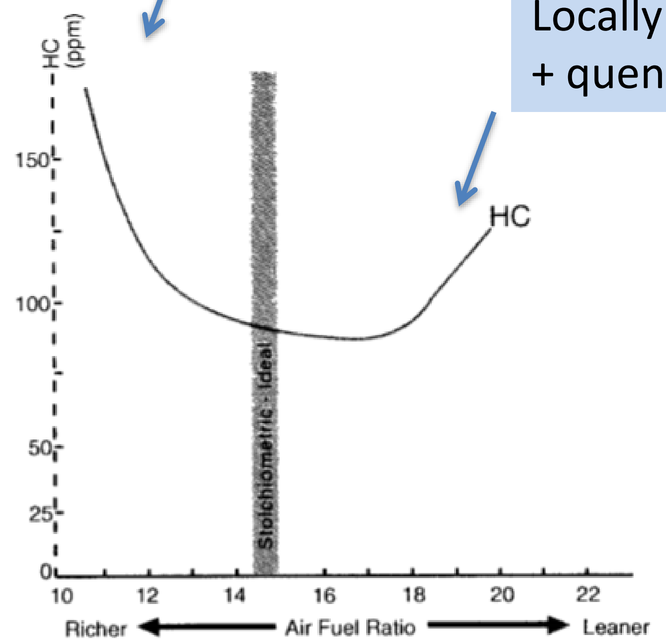
Emissions

No air enough
+quenching

$$C_\alpha H_\beta O_\gamma + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)(O_2 + 3.76N_2) \rightarrow$$
$$\frac{\alpha}{\phi}CO_2 + \frac{\beta}{2\phi}H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right)N_2 + \left(1 - \frac{1}{\phi}\right)C_\alpha H_\beta O_\gamma$$

Effects of A/F Ratio on Exhaust HC

As shown, exhaust HC production is lowest when A/F ratio is slightly leaner than "ideal"; however, HC's increases dramatically when the mixture becomes too rich or too lean to the point of misfire.



Locally no air enough
+ quenching

CO Emissions

CO emissions – carbon monoxide

$\lambda < 1$, rich conditions possible equation

$$C_xH_y+\lambda(x+y/4)*(O_2+3.76N_2)\Rightarrow aCO_2+cCO+dH_2O+eH_2+3.76*\lambda(x+y/4)*N_2$$

How many unknowns: **4**
From mass balance: **3 equations**
Use equilibrium reaction: water-gas shift equation and then **4 equations 4 unknowns**

CO Emissions

Water-gas shift reaction (WGS)

$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41.09$ kJ/mol

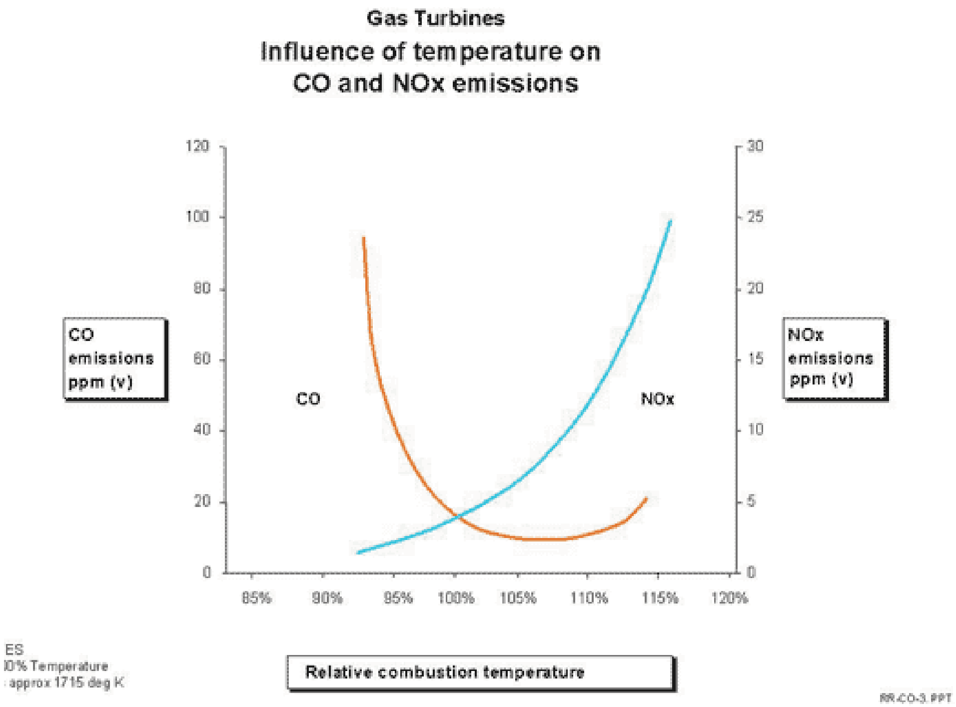
Low temperatures favours forward reaction

$CO + 1/2O_2 \rightleftharpoons CO_2$

High temperatures favours reverse reaction

Le Chatelier

Keq=kf/kr<1 the system tends to increase forward reaction



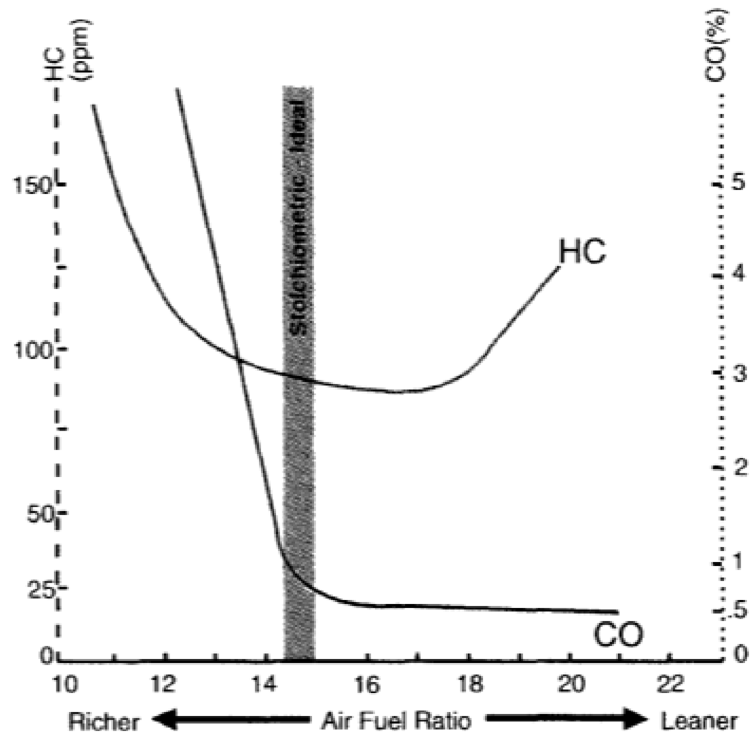
CO Emissions

CO emissions – carbon monoxide

$\lambda \ll 1$, rich conditions e.g. quenching

Effects of A/F Ratio on Exhaust CO

Exhaust CO is lowest when A/F ratio is leaner than "ideal"; however, CO increases dramatically with richer mixtures.

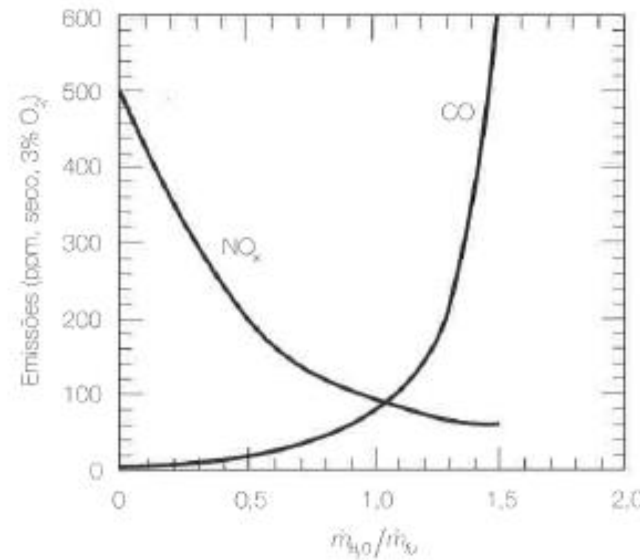


Emissions

Trade-off NOx / CO

CAPÍTULO 12 Combustão

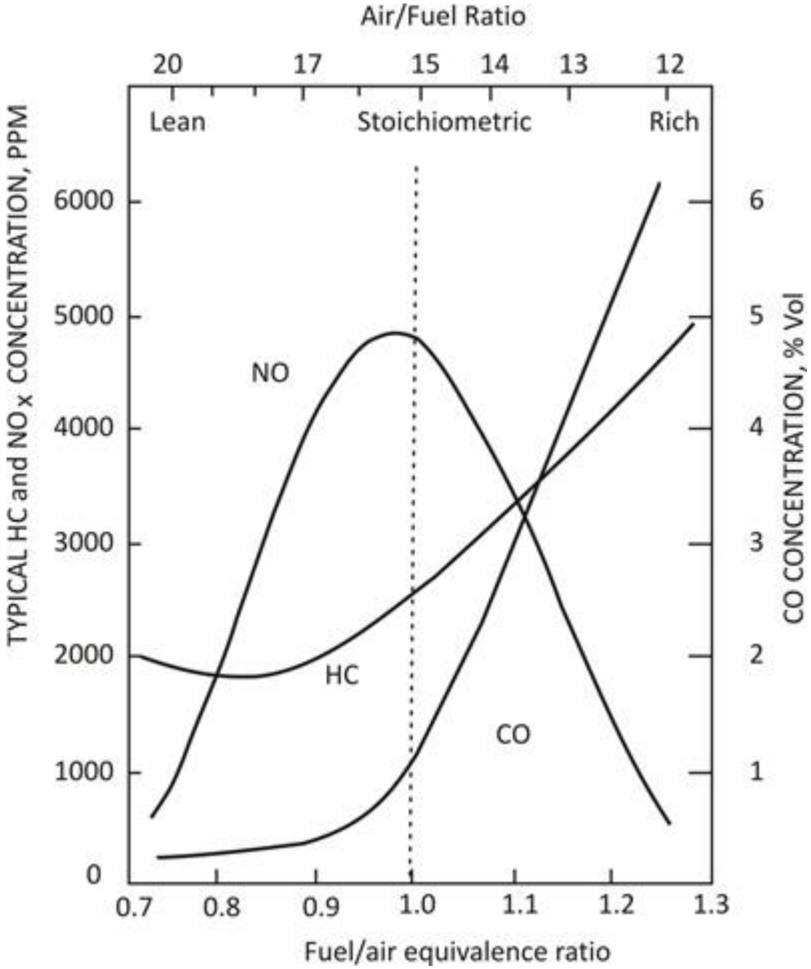
Figura 12.8 *Efeito da injecção de água nas emissões de NO_x e CO de turbinas a gás industriais. (Extraído de Bowman, 1992.)*

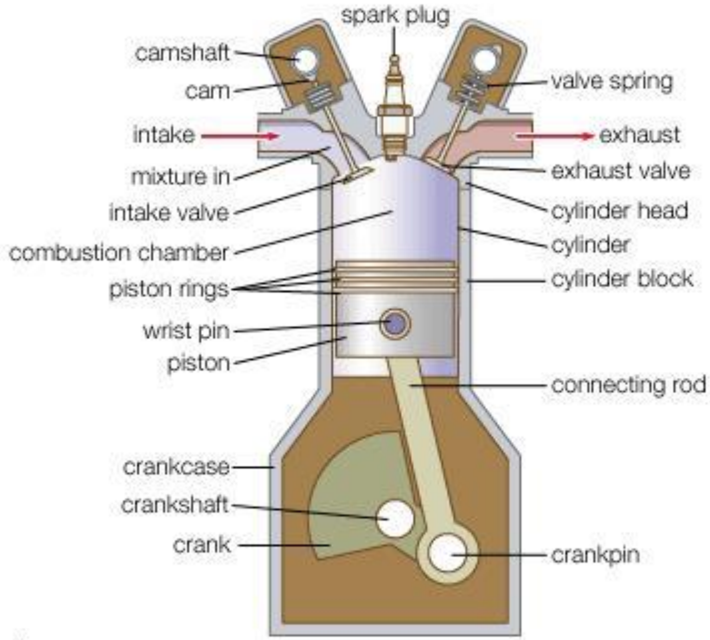


Effect of water injection industrial turbines

Typically lowering NOx imply increase other emissions

NOx, HC and CO





$$\phi = \frac{1}{\lambda}$$

NOx and VOC

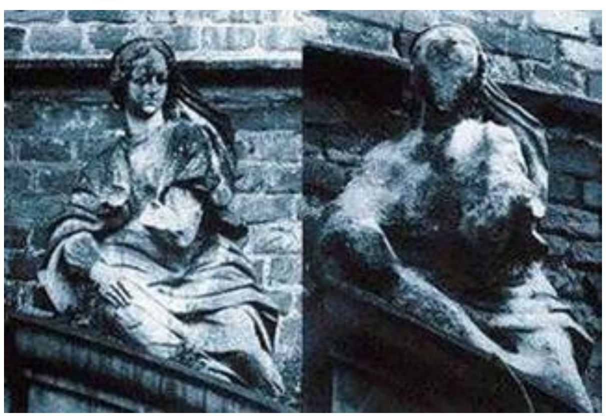
Problem: acid rain or smog (smoke+fog) problems

Nitic acid HNO_3

$2\,NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

$4\,NO + 3\,O_2 + 2\,H_2O \rightarrow 4\,HNO_3$

$4\,NO_2 + 2\,H_2O + O_2 \rightarrow 4\,HNO_3$



Tropospheric ozone O_3

$VOC + OH \xrightarrow{[O_2]} RO_2 + H_2O$

$CO + OH \xrightarrow{[O_2]} HO_2 + CO_2$

$RO_2 + NO \xrightarrow{[O_2]} \text{secondary VOC} + HO_2 + NO_2$

$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + NO \rightarrow NO_2 + O_2$

NOx and VOC

Problem: smog (smoke+fog) Shenzhen, China

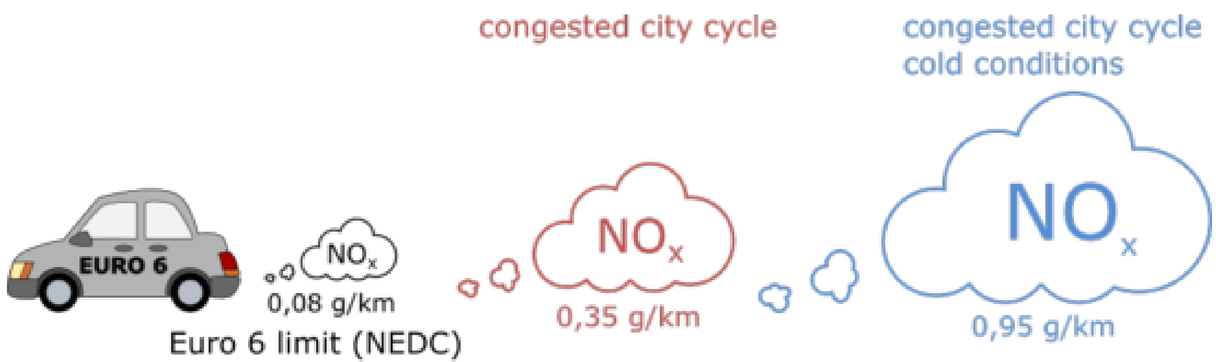
Aldehydes
Nitrogen oxides particularly nitric oxide and nitrogen oxide
Peroxyacetyl nitrate (PAN)
Tropospheric ozone
Volatile organic compound

$C_2H_3NO_5$
(PAN)
O_3 (Main)
VOC

NOx

Adiabatic flame temperature ↑

NOx emissions ↑



Chemical Equilibrium

P#9 Consider the combustion of C7H14 (~diesel). Determine the emission concentration of CO (ppm) in both cases.

a) At 1200 K and 10 atm with A/F=40;

b) At 2400 K, 40% of theoretical stoichiometric air.

Thermochemistry

P#10 Following table list the results of an experiment of boiler that is used to produce superheated vapour. The boiler is feed by natural gas trough a conventional burner.

a) The air/fuel ratio
b) The higher heating value of the fuel
c) Heat transfer to water, assuming that heat loss trough boiler walls are 3% of the lower heating value.

Fuel rate	**150 m^3/h**
Reactants temperature@ entrance	25°C
Products temperature @exit	227°C
Fuel composition by volume(%)	CH_4: 88 H_2: 2 CO_2: 3 N_2: 7
Dry analysis combustion products (%)	O_2: 1.1 CO_2: 10.8 N_2: 88.1

Obrigado

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