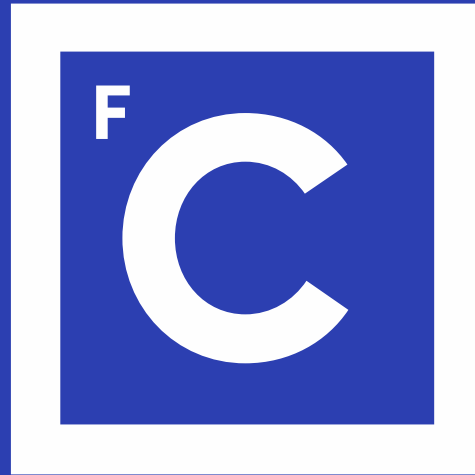




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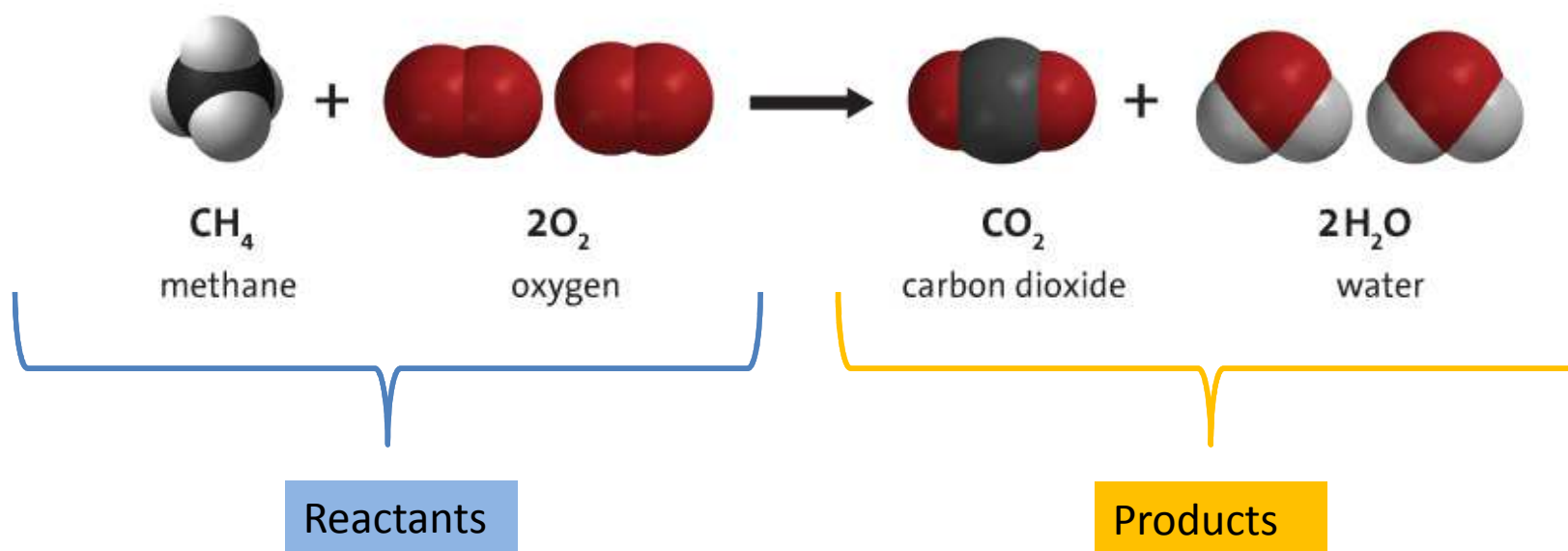
DISCIPLINA MIEA 2018

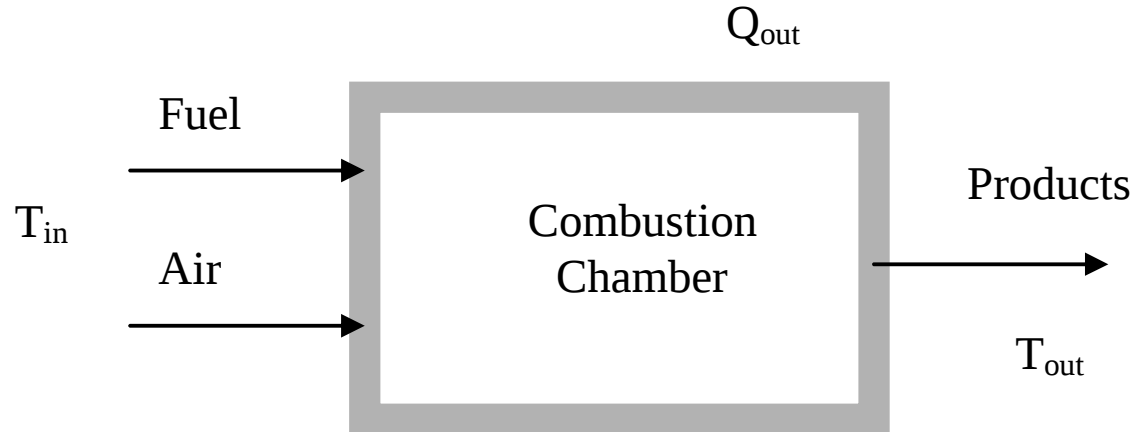


Technologies of combustion

Corpo docente

Carla Silva (Teóricas e práticas) /Theory and practice
camsilva@ciencias.ulisboa.pt





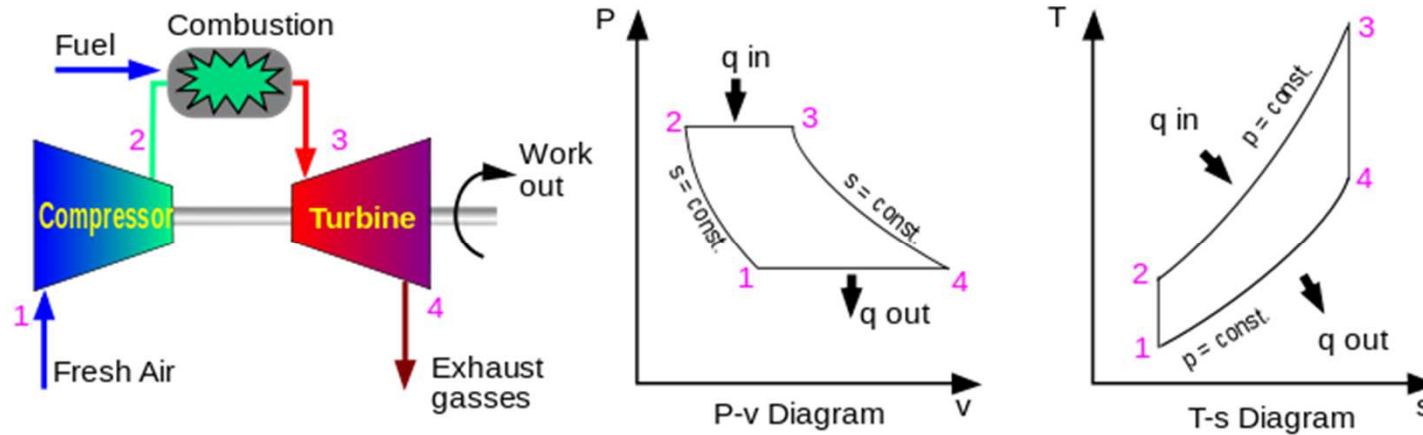
- Maximum heat release, $\max Q_{\text{out}}: T_{\text{out}} = T_{\text{in}}$
- Maximum flame temperature, T_{ad} :

$H_{\text{reag}}(T_{\text{in}}) = H_{\text{prod}}(T_{\text{ad}})$ (constant pressure, e.g. Diesel engine, gas turbine, furnace)

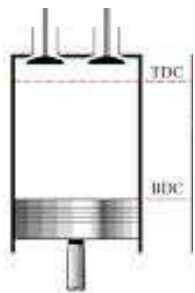
$H_{\text{reag}}(T_{\text{in}}) = H_{\text{prod}}(T_{\text{ad}}) - R(n_{\text{prod}} T_{\text{ad}} - n_{\text{reag}} T_{\text{in}})$ (constant volume, e.g. gasoline engine)

$H_{\text{reag}}(T_{\text{in}}) = H_{\text{prod}}(T_{\text{ad}})$ (constant pressure, e.g. Diesel engine, **gas turbine**, furnace)

Brayton cycle



$$H_{\text{reag}}(T_{\text{in}}) = H_{\text{prod}}(T_{\text{ad}}) - R(n_{\text{prod}}T_{\text{ad}} - n_{\text{reag}}T_{\text{in}}) \quad (\text{constant volume, e.g. gasoline engine})$$

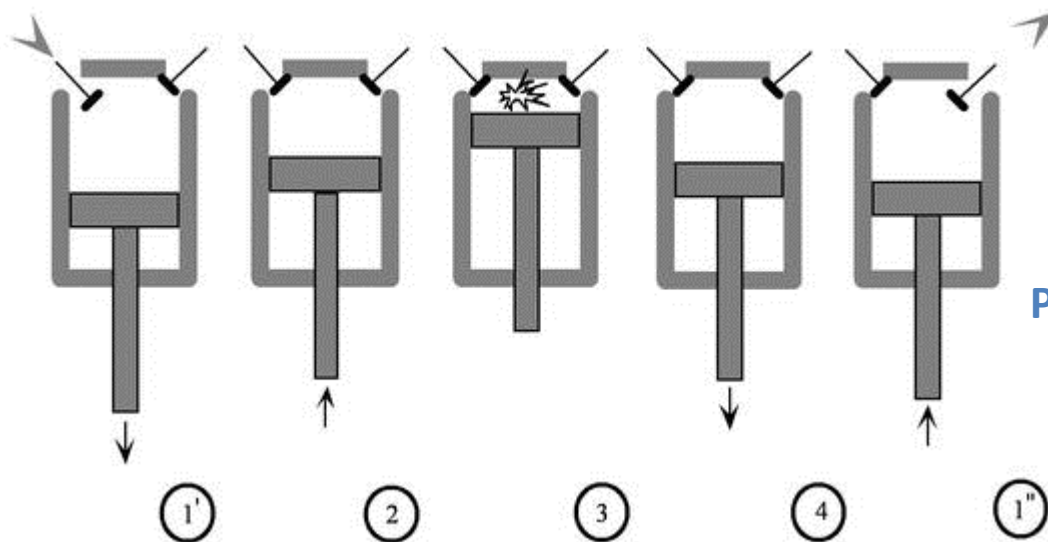


Top Dead Centre

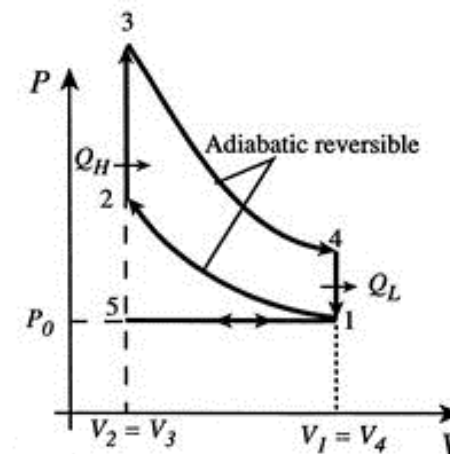
- *Ponto morto superior*

Bottom Dead Centre

- *Ponto morto inferior*



Otto cycle



Ponto morto superior

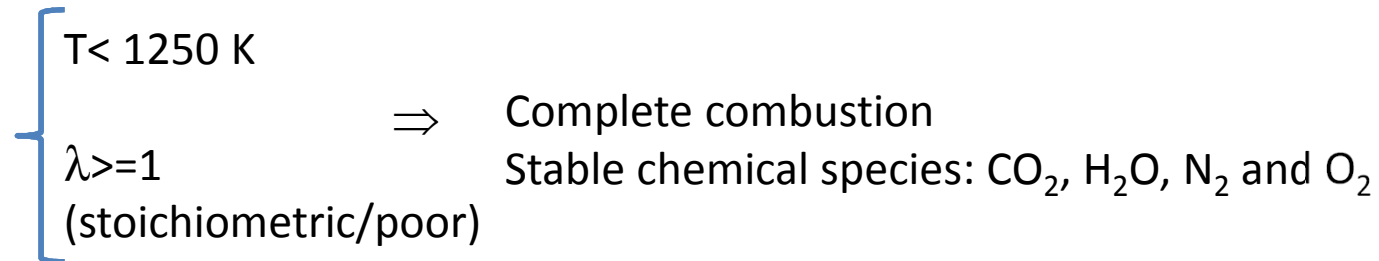
Ponto morto inferior

Chemical equilibrium

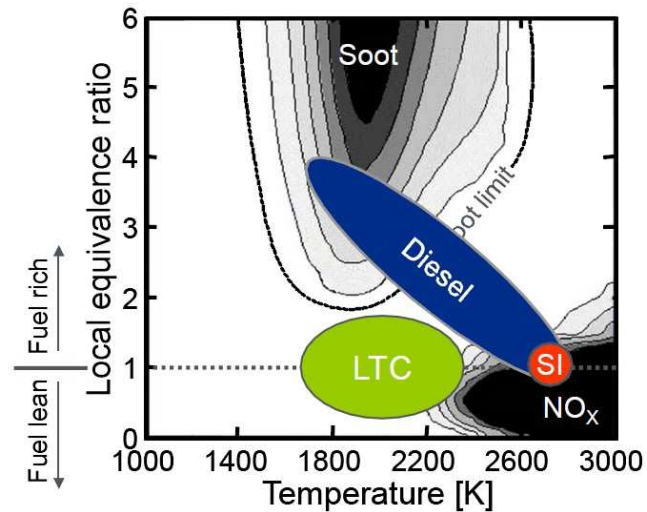
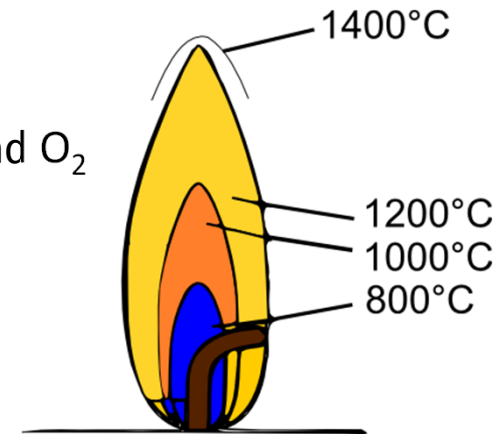


Chemical equilibrium is the state reached when the concentrations of the products and reactants **remain constant over time**. The mixture of reactants and products in the equilibrium state is the **equilibrium mixture**.

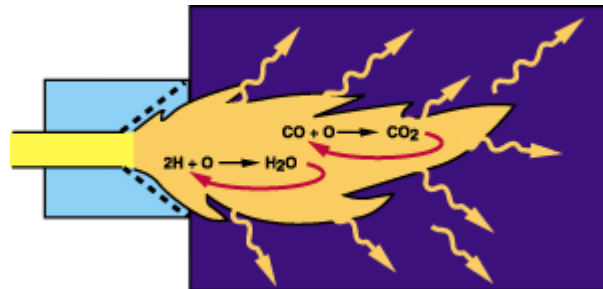
Chemical equilibrium



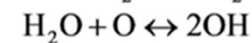
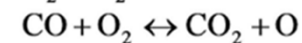
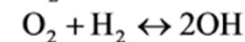
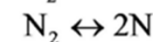
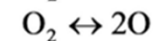
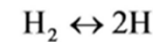
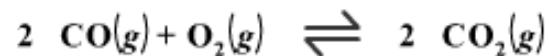
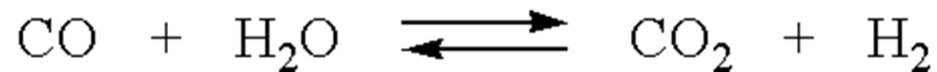
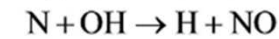
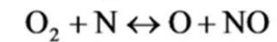
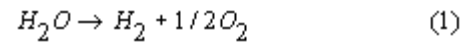
Usually temperatures are higher than 1250 K.....e.g.



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

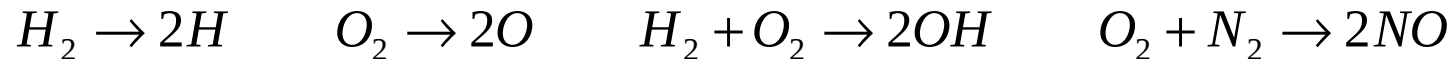


Chemical Reactions



Chemical Equilibrium

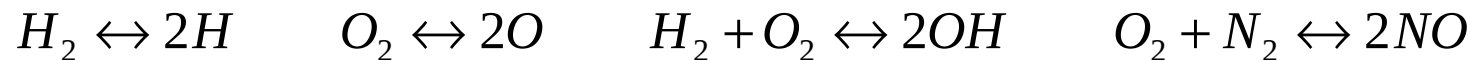
- In general the combustion products consist of more than just CO_2 , H_2O and N_2
- For rich mixtures CO also exists in the products and at high temperatures the molecules dissociate to form H , O , OH , NO via the following reactions:



- The opposite direction reactions are also possible



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

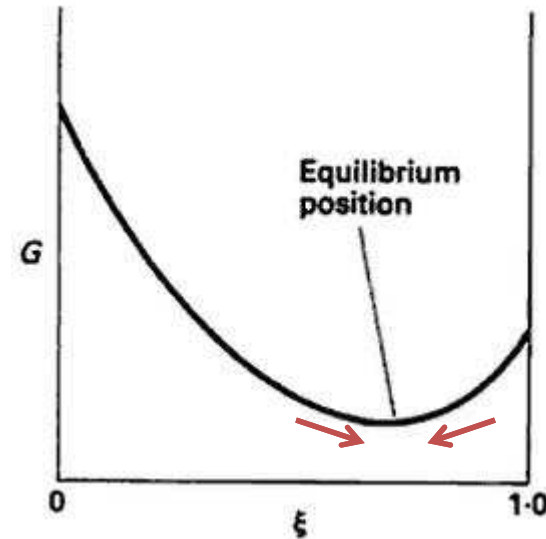


Chemical Equilibrium

$G = H - TS$ Free Gibbs Energy

@equilibrium, $dG = 0$

$$K = \exp \left[-\frac{\Delta G^0(T)}{RT} \right] = \frac{p_A^{n_A} \cdot p_B^{n_B}}{p_C^{n_C} \cdot p_D^{n_D}}$$



Le chatelier

Chemical equilibrium and 2nd law thermodynamics

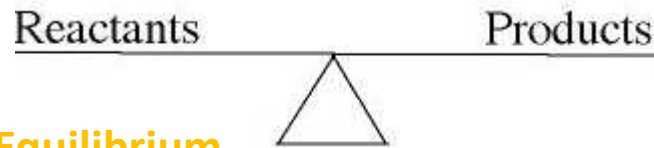
$$\Delta S = \oint \frac{\partial Q}{T} + \sigma$$

$\sigma \geq 0$ entropy generation

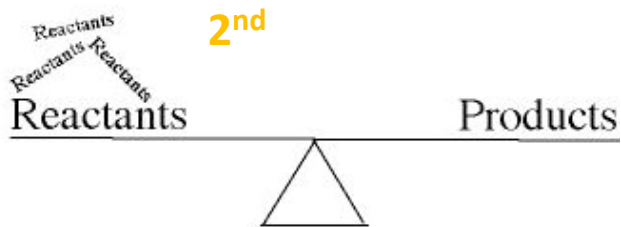
T = control volume
temperature

$G = H - TS$ Free Gibbs Energy

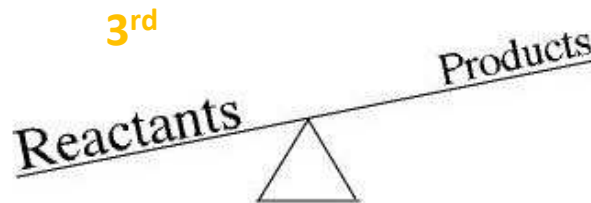
Le chatelier



1st Equilibrium

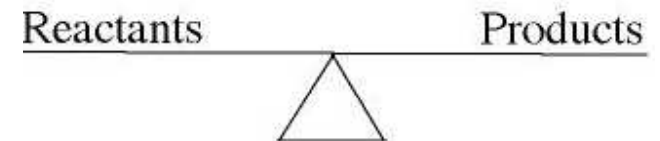


2nd

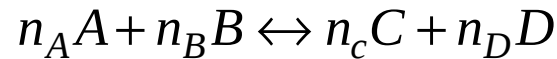


3rd

4th Equilibrium again



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



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

$$K_p \quad \frac{k_f}{k_r} = \exp \left[-\frac{\Delta G^0(T)}{RT} \right] = \frac{p_A^{n_A} \cdot p_B^{n_B}}{p_C^{n_C} \cdot p_D^{n_D}}$$

K is the **equilibrium constant**

K_c

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

Forward reaction Reverse reaction

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

K is the **equilibrium constant**

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

$$\underset{\substack{\uparrow \\ \text{Forward reaction}}}{k_f(T)} / \underset{\substack{\uparrow \\ \text{Reverse reaction}}}{k_r(T)} = K_p(T) = \frac{X_C^{n_C} \cdot X_D^{n_D}}{X_A^{n_A} \cdot X_B^{n_B}} \left(\frac{P}{P_{ref}} \right)^{n_C + n_D - n_A - n_B}$$

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

mol/m³

K is the **equilibrium constant**

K_n

Forward reaction  $k_f(T) / k_r(T) = K_n(T) = \frac{n_C^{n_C} \cdot n_D^{n_D}}{n_A^{n_A} \cdot n_B^{n_B}}$  Reverse reaction

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

K is the **equilibrium constant**

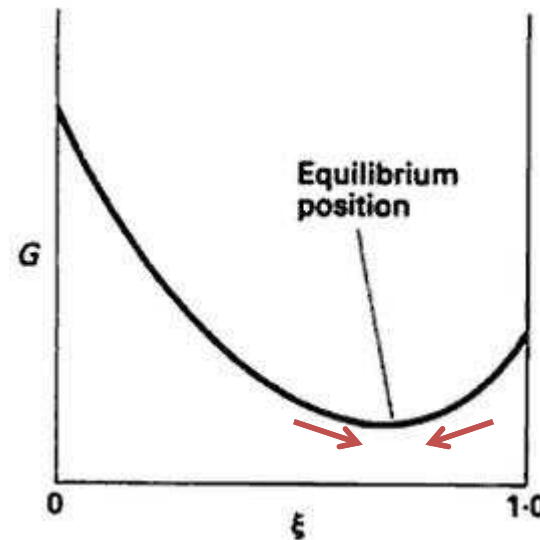
$$K_p = K_c * \left(\frac{RT}{P_{ref}} \right)^{n_{prod} - n_{reag}} = K_n * \left(\frac{P}{n_{Total} P_{ref}} \right)^{n_{prod} - n_{reag}}$$

P em bar

$G = H - TS$ Free Gibbs Energy

@equilibrium, $dG = 0$

$$K = \exp \left[- \frac{\Delta G^0(T)}{RT} \right] = \frac{p_A^{n_A} \cdot p_B^{n_B}}{p_C^{n_C} \cdot p_D^{n_D}}$$



Le chatelier

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

APÊNDICE 4
CONSTANTES DE EQUILÍBRIO

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

$\log_{10} K_p$ com as pressões parciais em atmosferas

$T (K)$	$\frac{p_{H_2O}}{p_{H_2} \sqrt{p_{O_2}}}$	$\frac{p_{CO_2}}{p_{CO} \sqrt{p_{O_2}}}$	$\frac{(p_{H_2O})(p_{CO})}{(p_{H_2})(p_{CO_2})}$	$\frac{p_{H_2O}}{p_{CH} \sqrt{p_{H_2}}}$	$\frac{p_{NO}}{\sqrt{p_{O_2}} \sqrt{p_{N_2}}}$	$\frac{p_{H_2}}{(p_H)^2}$	$\frac{p_{O_2}}{(p_O)^2}$	$\frac{p_{N_2}}{(p_N)^2}$
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

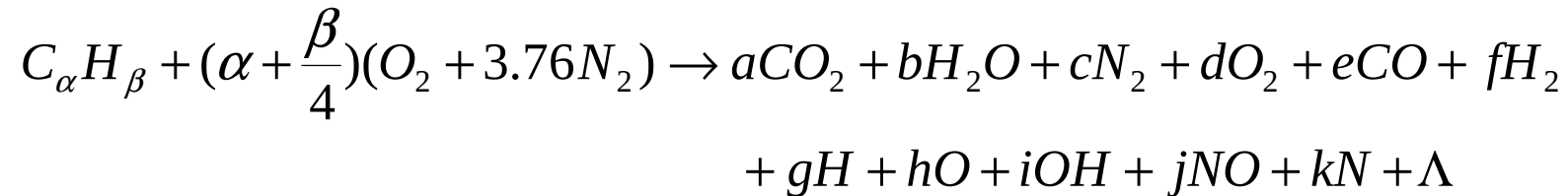
Tabela A4.1

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

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.

- 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.



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:

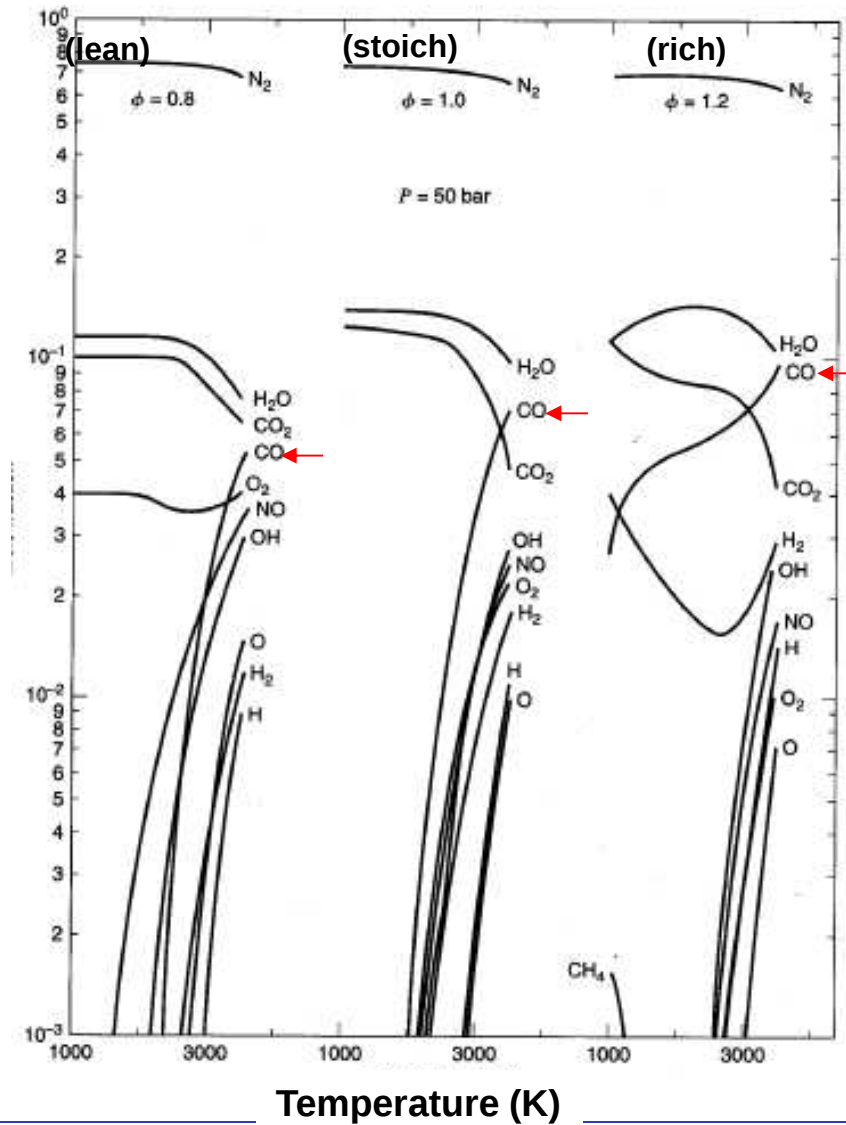
June 1996



Composition of Octane-air Mixtures at Equilibrium

C₈H₁₈

Mole fraction of each species





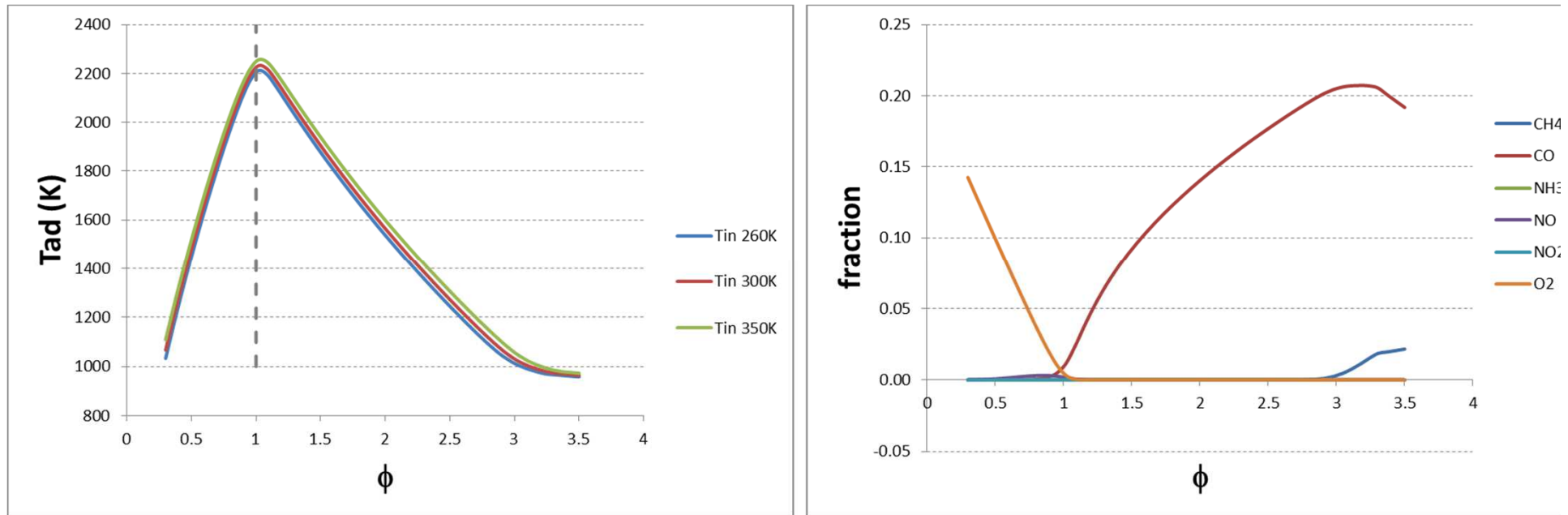
Cantera

Chemical Kinetics • Thermodynamics • Transport Processes

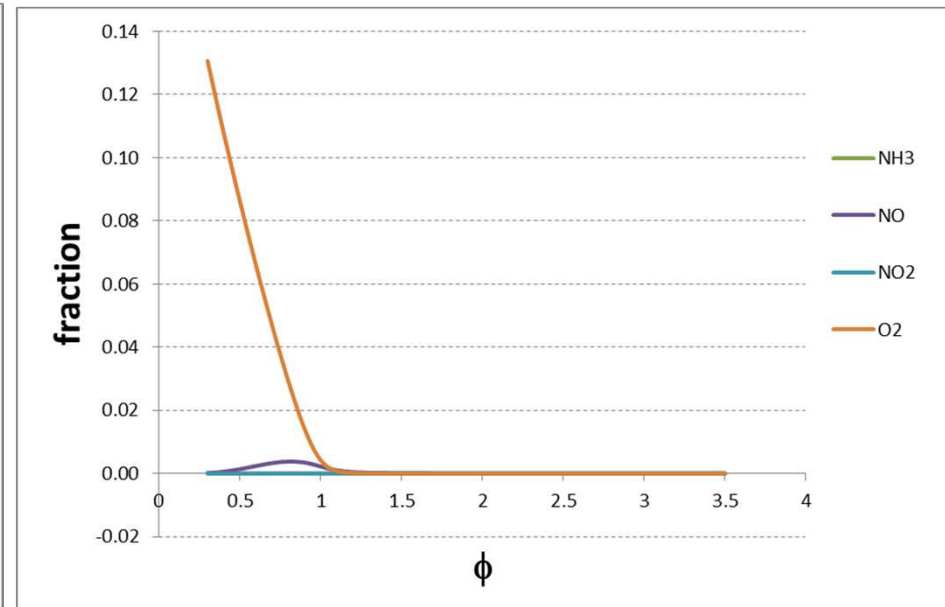
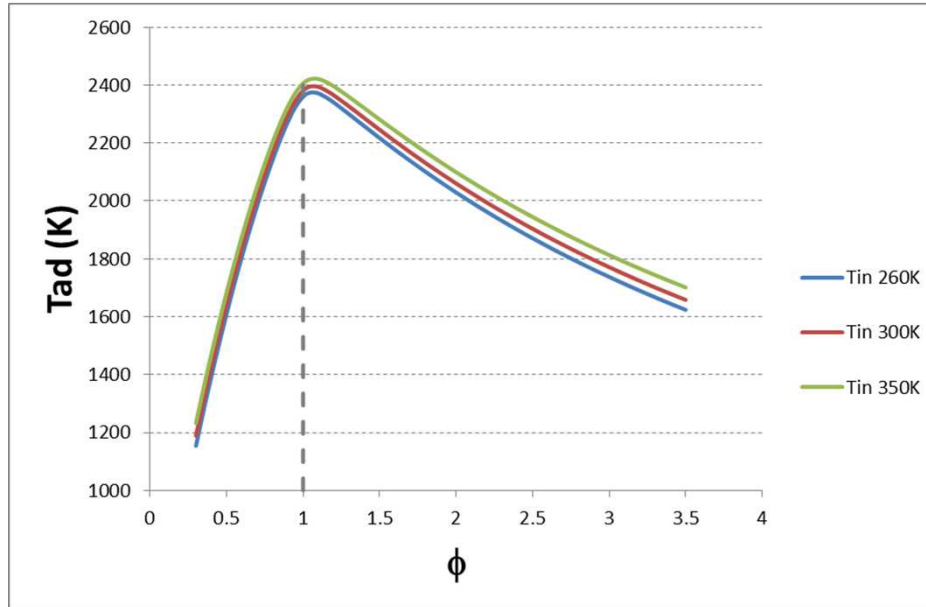


CONDA

http://www.cantera.org/docs/sphinx/html/cython/examples/multi-phase_adiabatic.html

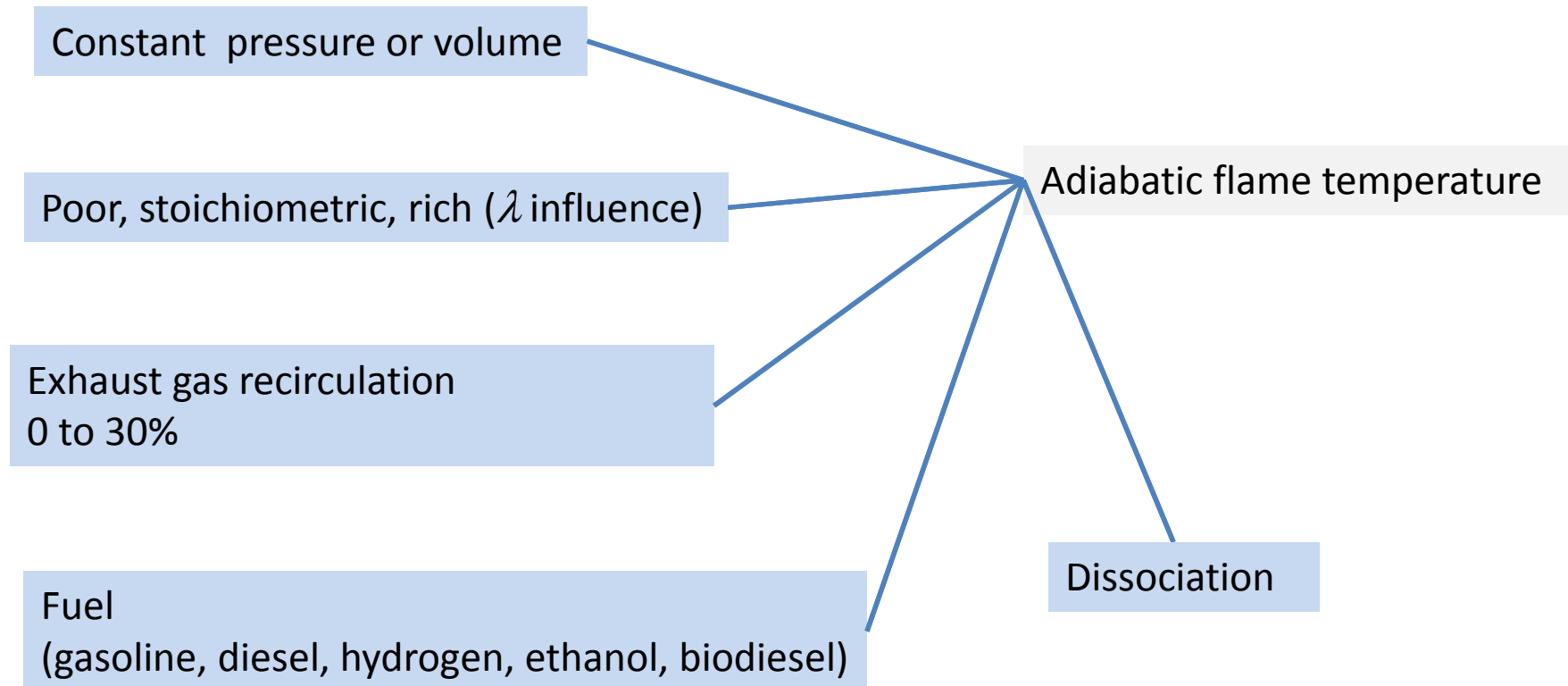


http://www.cantera.org/docs/sphinx/html/cython/examples/multi-phase_adiabatic.html



http://www.cantera.org/docs/sphinx/html/cython/examples/multi-phase_adiabatic.html

1st assignment: Flame Temperature Analysis and NOx Emissions for different Fuels and combustion conditions



Adiabatic???

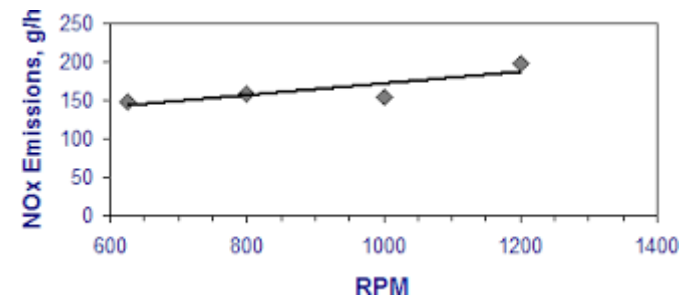
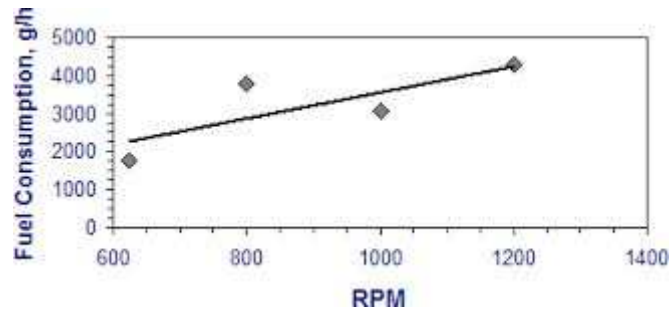
Combustion reactions generally occur very fast $\sim 1\text{ms}$

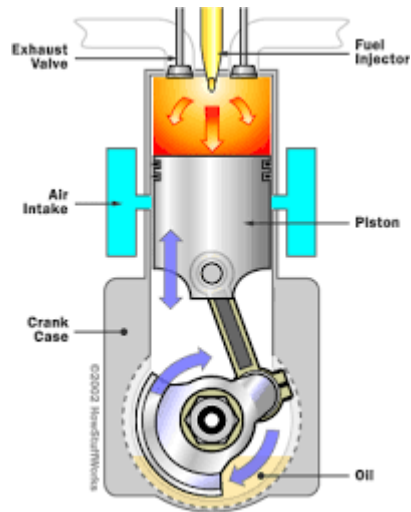
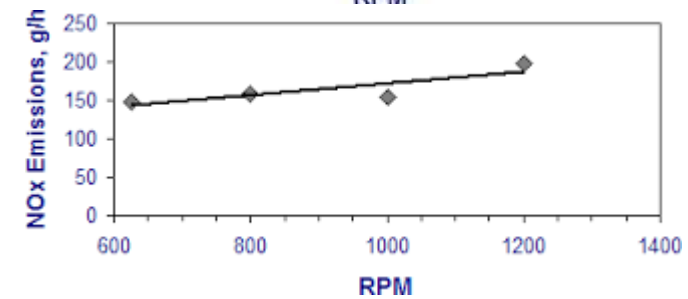
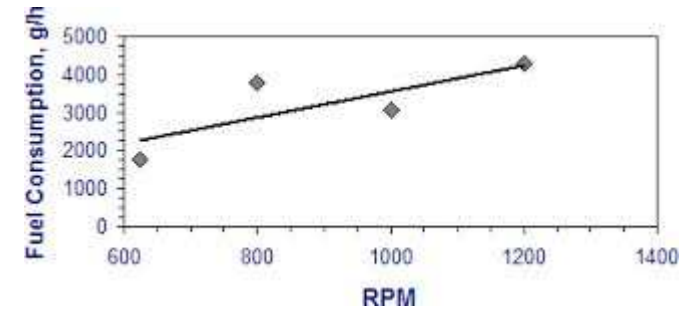


Little heat or work transfer takes place



Maximum temperature achieved is often near T_{ad}

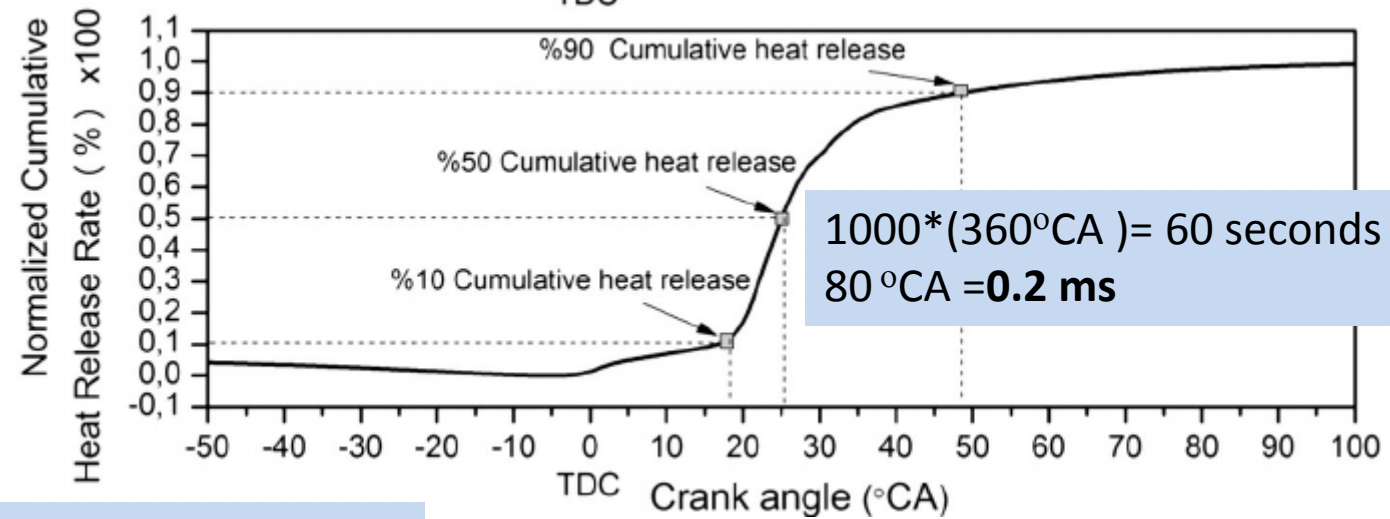
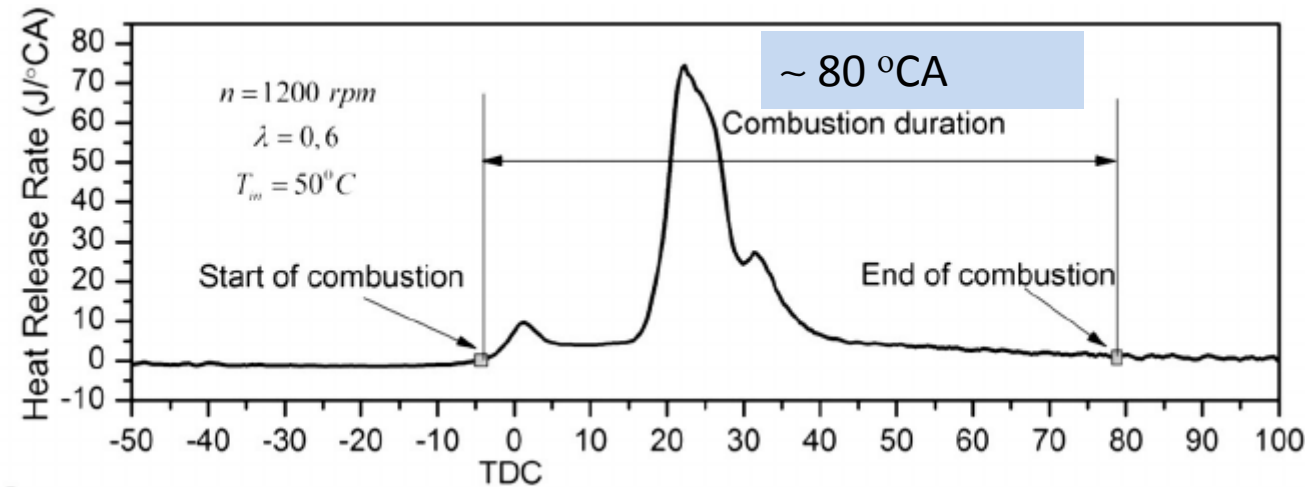
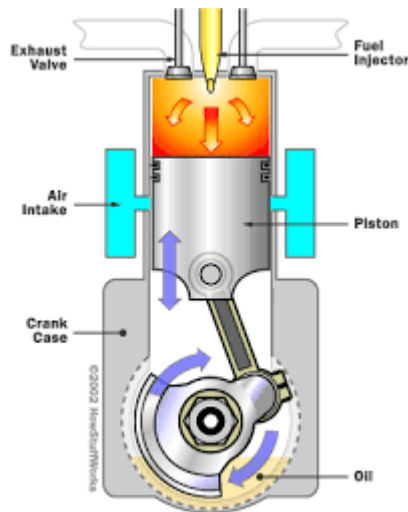




1000 rpm= 1000 revolutions per minute

1 revolution is 360°CA (Crank angle)

$1000 \times (360^\circ \text{CA}) = 60 \text{ seconds}$



More rpm, less combustion time!!!

NO_x means the sum of NO and NO₂ contents in flue gas recalculated on NO₂
NO_x = NO + NO₂ (expressed in NO₂)

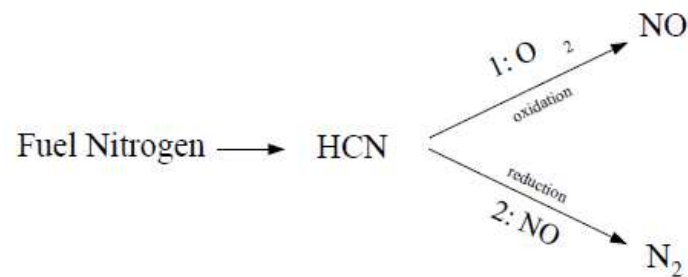
$$\text{NO}_x [\text{ppm}] = \text{NO} [\text{ppm}] + \text{NO}_2 [\text{ppm}]$$

The NO_x content in the combustion gases from conventional power plant boilers and many industrial heating process contains some **90 % NO** with the remainder NO₂

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

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

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



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

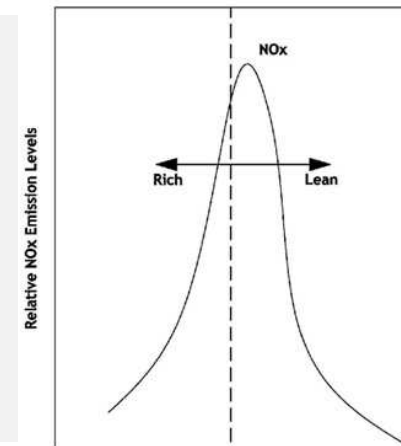
	<----- Low Rank ----->		<----- High Rank ----->	
Rank:	Lignite	Subbituminous	Bituminous	Anthracite
Age:	increases			
% Carbon:	65-72	72-76	76-90	90-95
% Hydrogen:	~5	decreases		~2
% Nitrogen:	~1-2			
% Oxygen:	~30	decreases		~1
% Sulfur:	~0	increases	~4	decreases ~0
%Water:	70-30	30-10	10-5	~5
Heating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

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

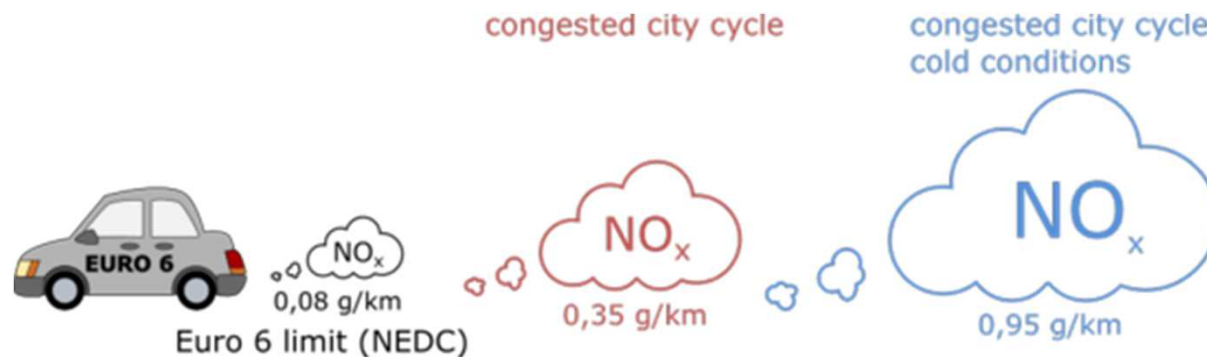
@<http://www.ems.psu.edu/~radovic/Chapter7.pdf>

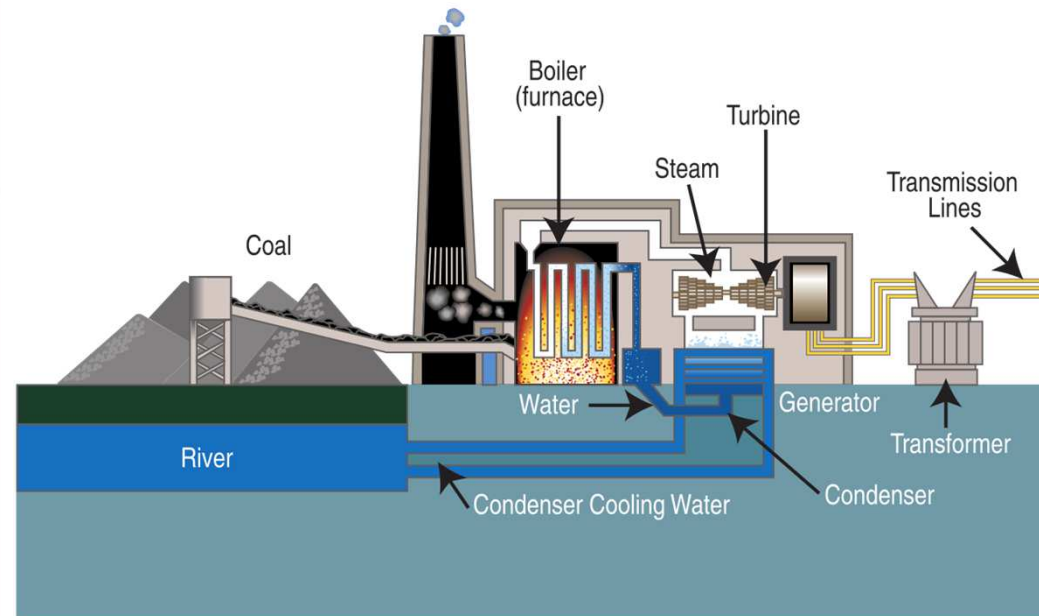
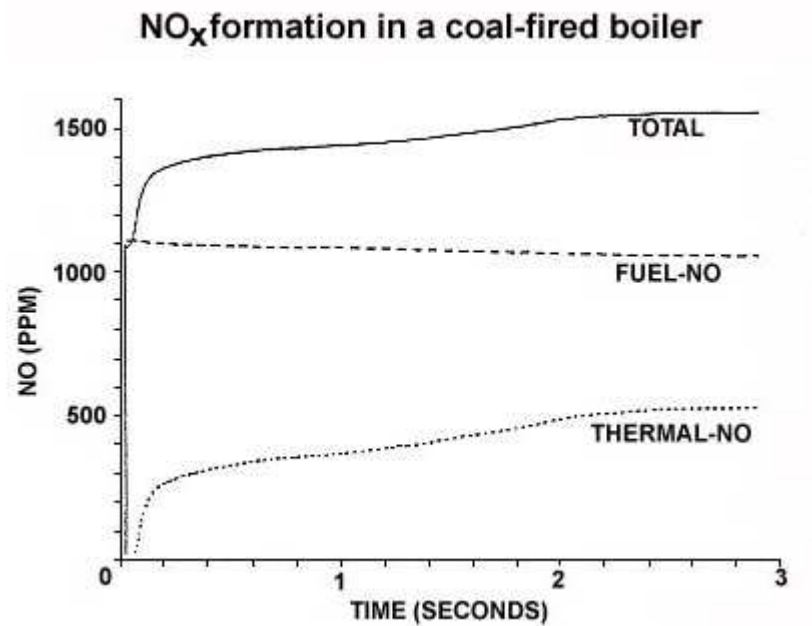
The conversion of fuel N is weakly temperature dependent but depends strongly upon local burner stoichiometry.

Impact of Pulverizer Performance on Nitrous Oxide Emissions



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





ppm ☺ !!!!

Exhaust gas recirculation and aftertreatment (lean combustion)

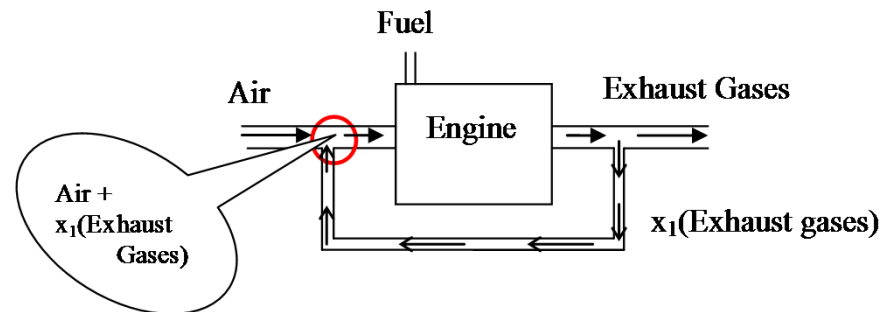
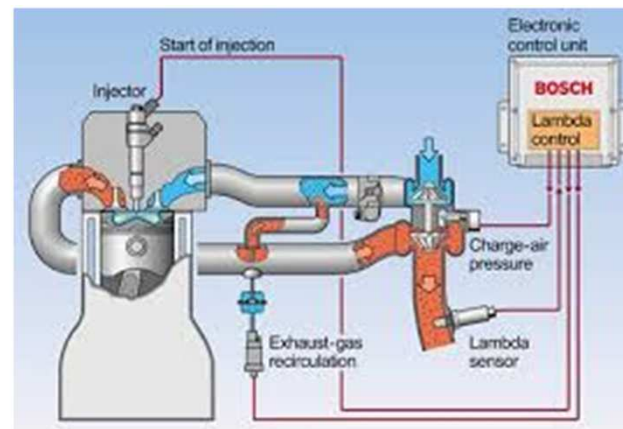
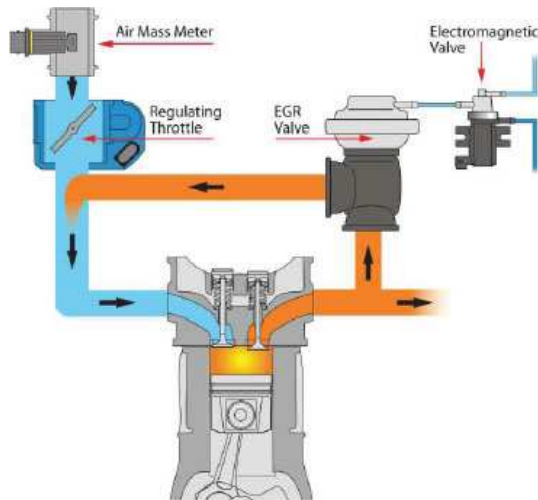
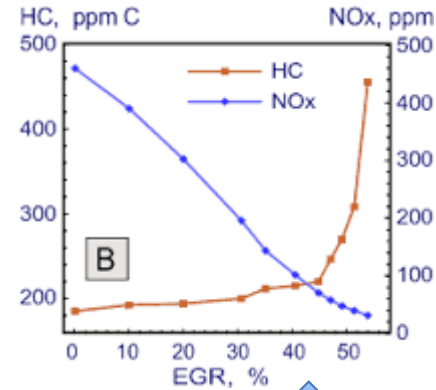
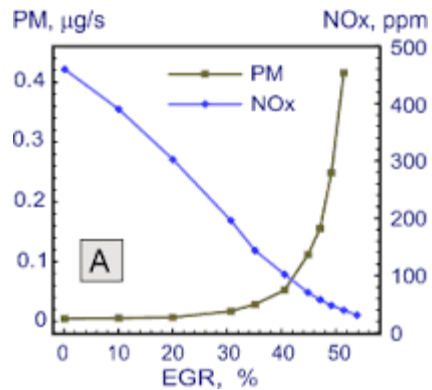


Figure 2: Exhaust Gas Re- circulation



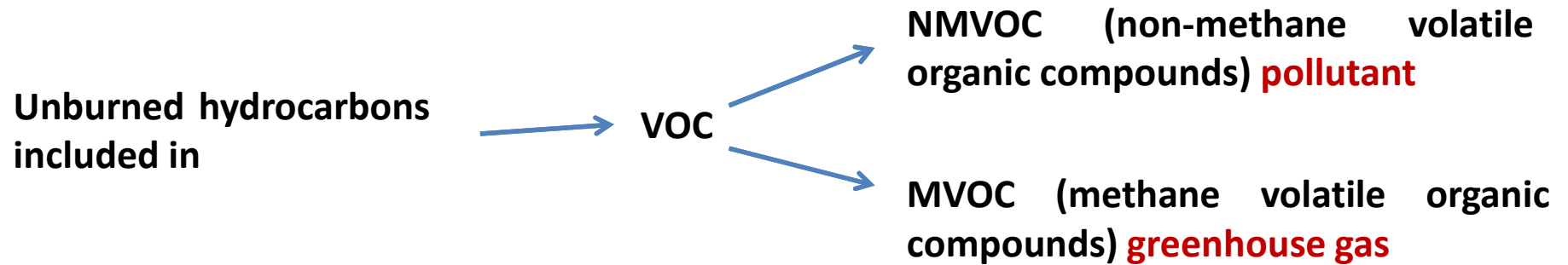
EGR influence Emissions

Exhaust gas recirculation and aftertreatment

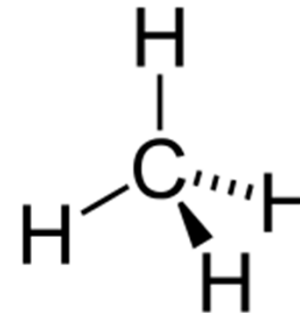


Objective: minimize emissions

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



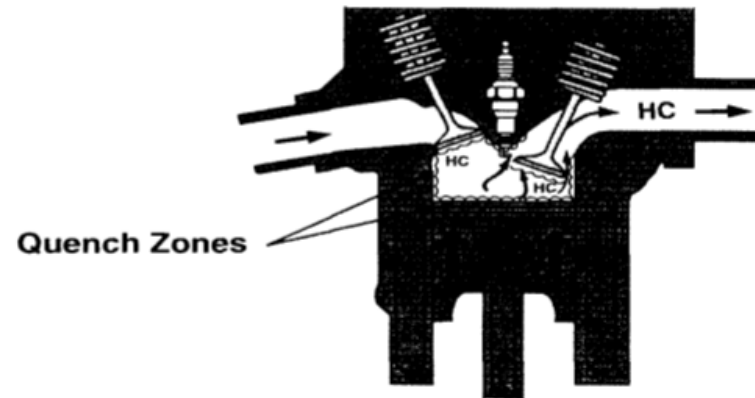
Organic compounds are a class of complex molecules that are characterized by their use of carbon as a molecular backbone



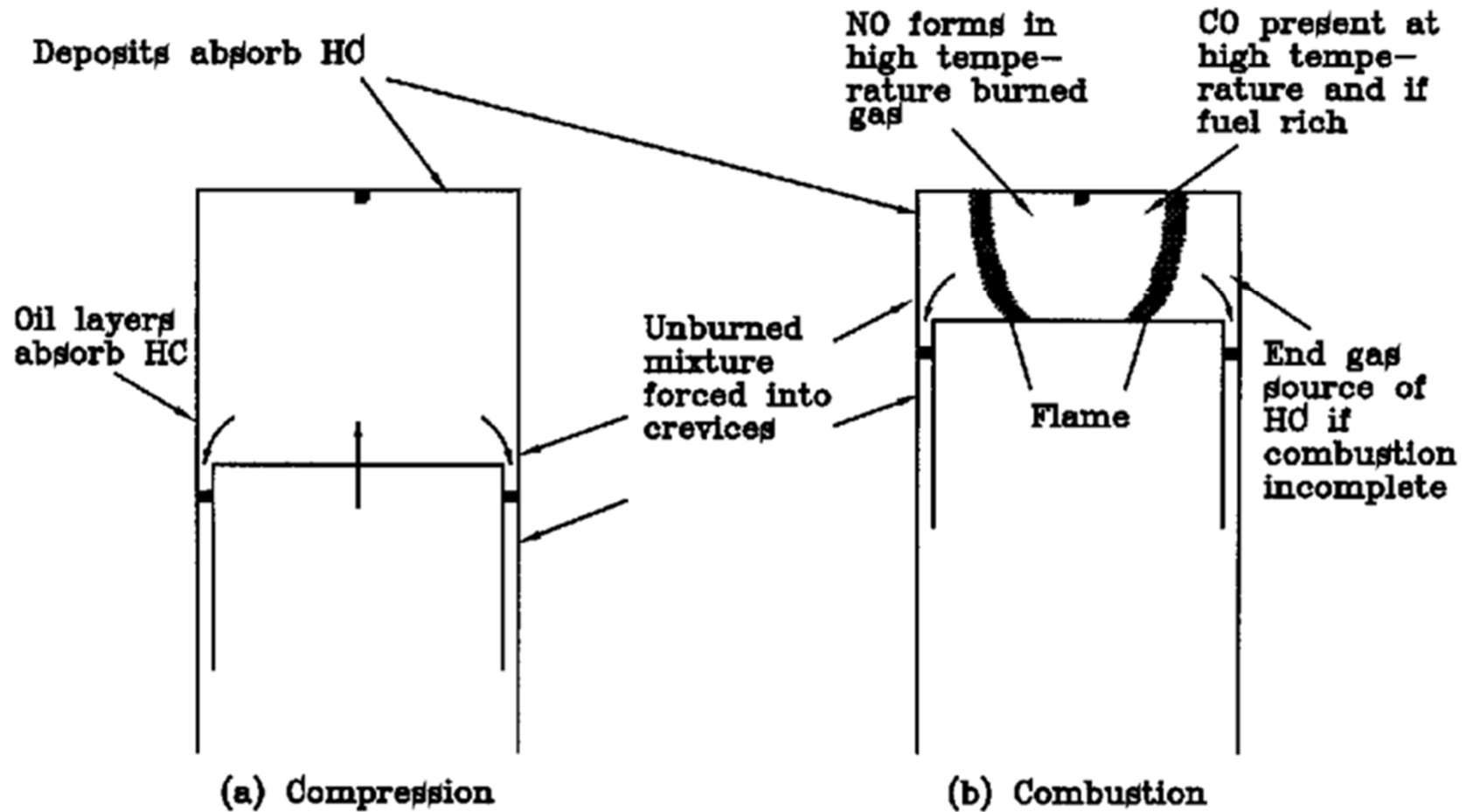
Unburned hydrocarbons

"Quenching"

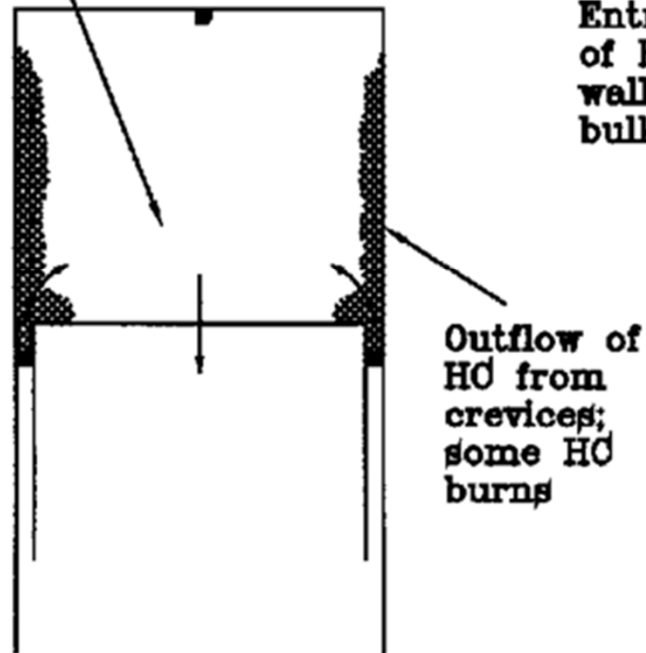
Quenching occurs when the combustion flame-front is extinguished before all the fuel is burned.



Wall quenching



As burned gases cool,
first NO chemistry, then
CO chemistry freezes



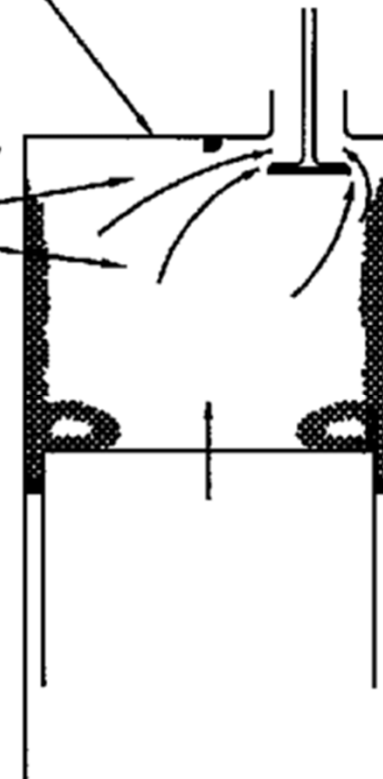
(c) Expansion

Deposits absorb HC

Entrainment
of HC from
wall into
bulk gas

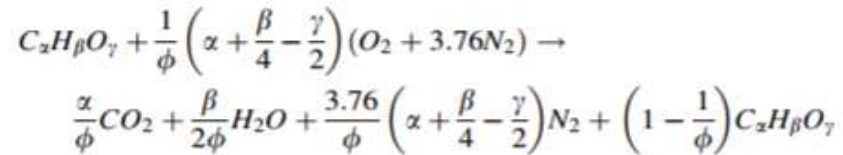
Oil layers
absorb HC

Piston
scrapes
HC off
walls



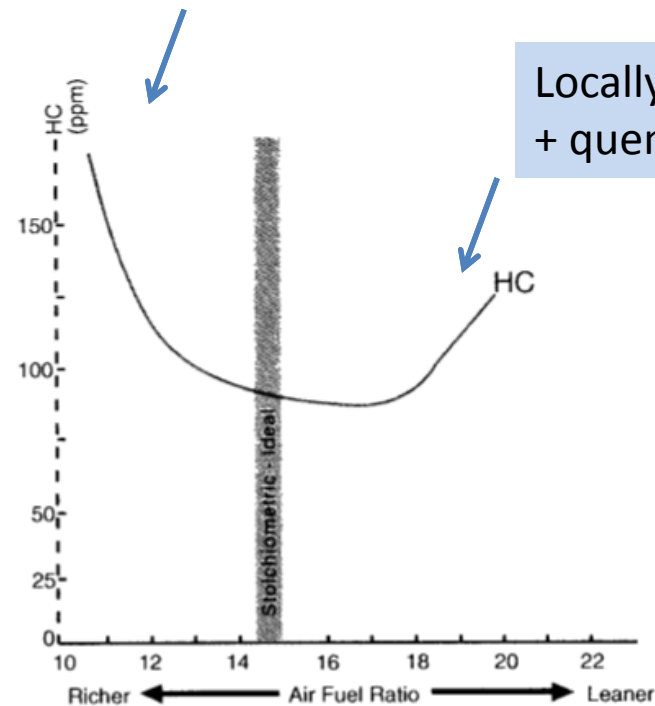
(d) Exhaust

No air enough
+ quenching



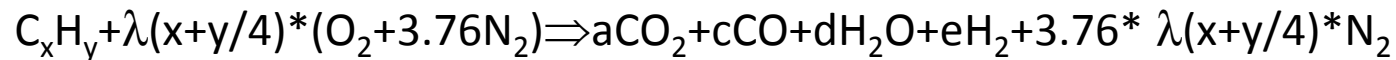
Effects of A/F Ratio on Exhaust HC

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



CO emissions – carbon monoxide

$\lambda < 1$, rich conditions possible equation

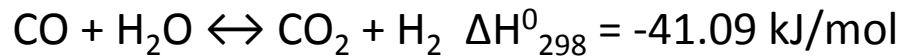


How many unknowns: **4**

From mass balance: **3 equations**

Use equilibrium reaction: water-gas shift equation and then **4 equations 4 unknowns**

Water-gas shift reaction (WGS, no dissociation)



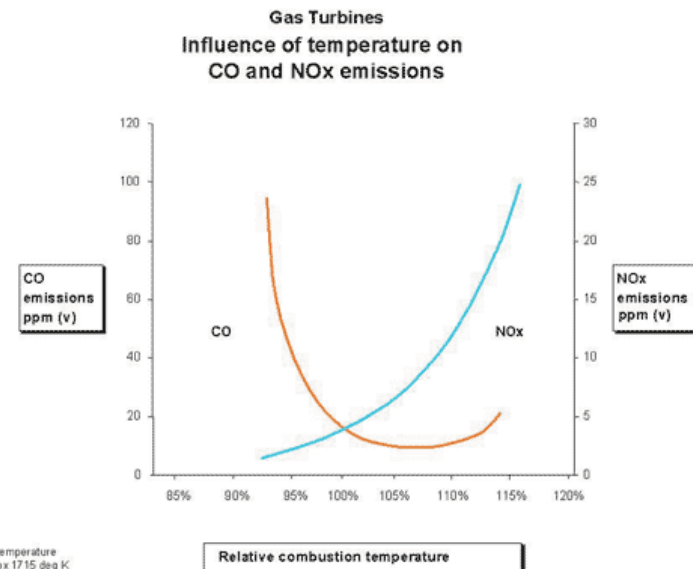
Low temperatures favours forward reaction



High temperatures favours reverse reaction

Le Chatelier

$K_{eq} = k_f/k_r < 1$ the system tends to increase forward reaction

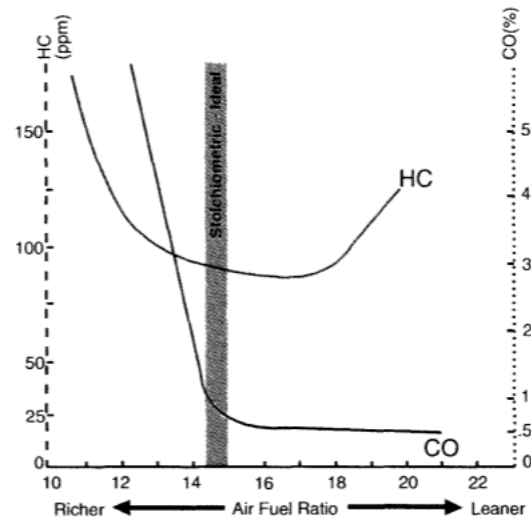


CO emissions – carbon monoxide

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

Effects of A/F Ratio on Exhaust CO

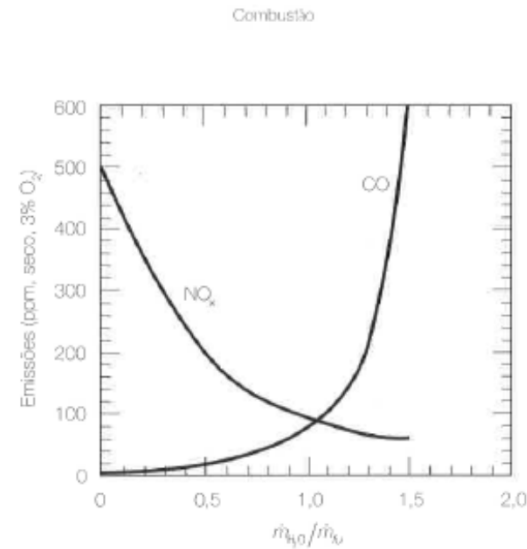
Exhaust CO is lowest when A/F ratio is leaner than "ideal"; however, CO increases dramatically with richer mixtures.



Trade-off NOx / CO

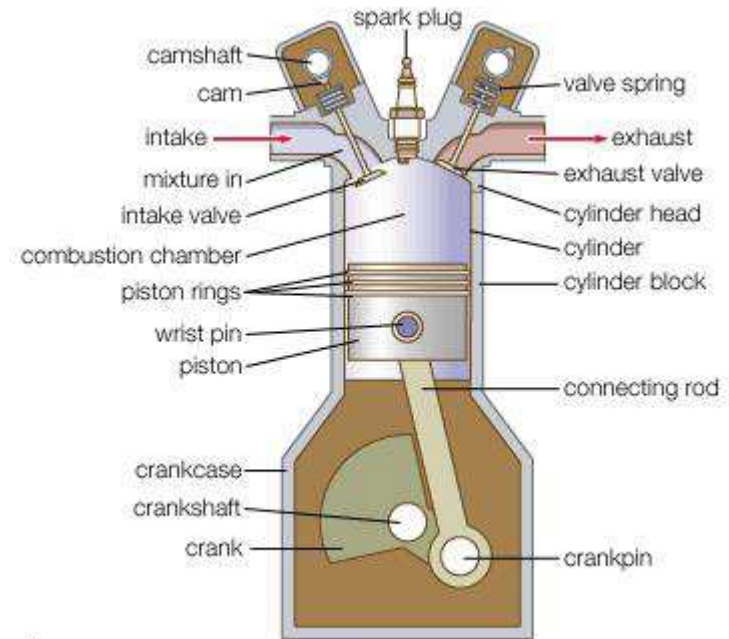
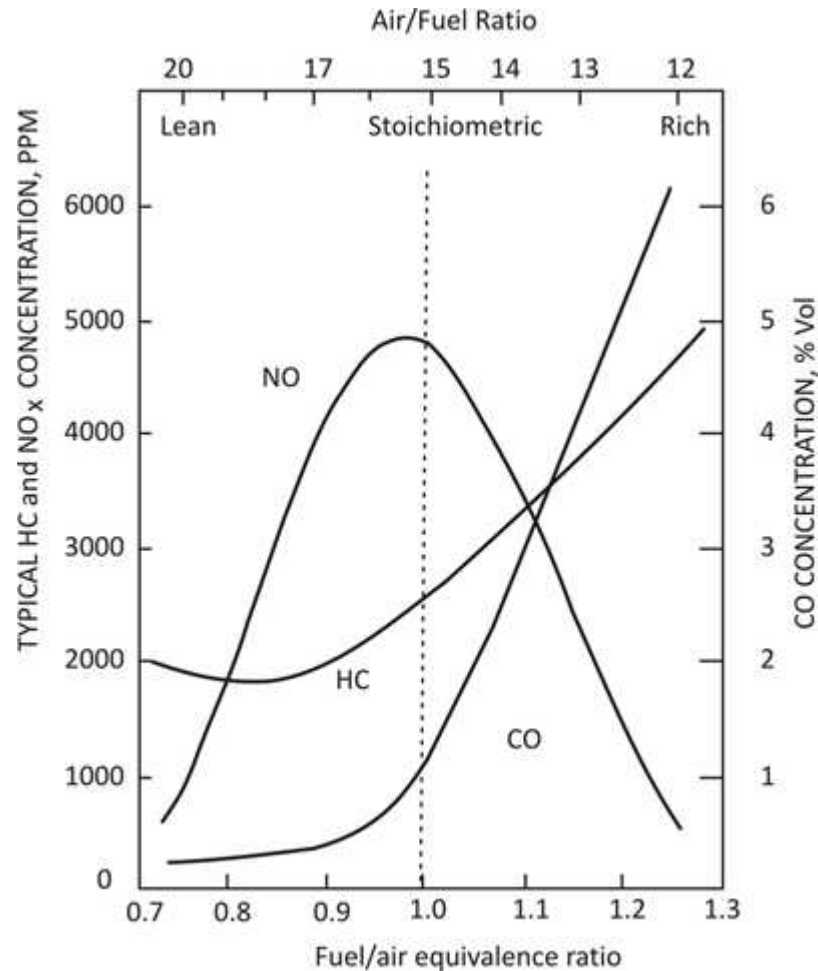
CAPÍTULO 12

Figura 12.8
 Efeito da injeção 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

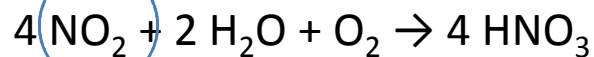
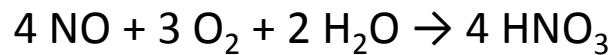
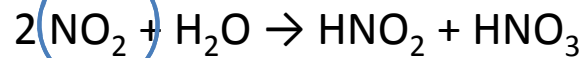


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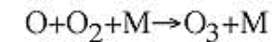
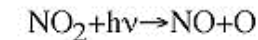
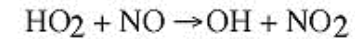
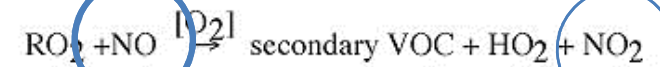
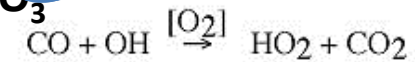
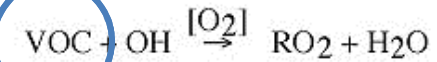
$$\phi = \frac{1}{\lambda}$$

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

Nitric acid HNO_3



Tropospheric ozone O_3



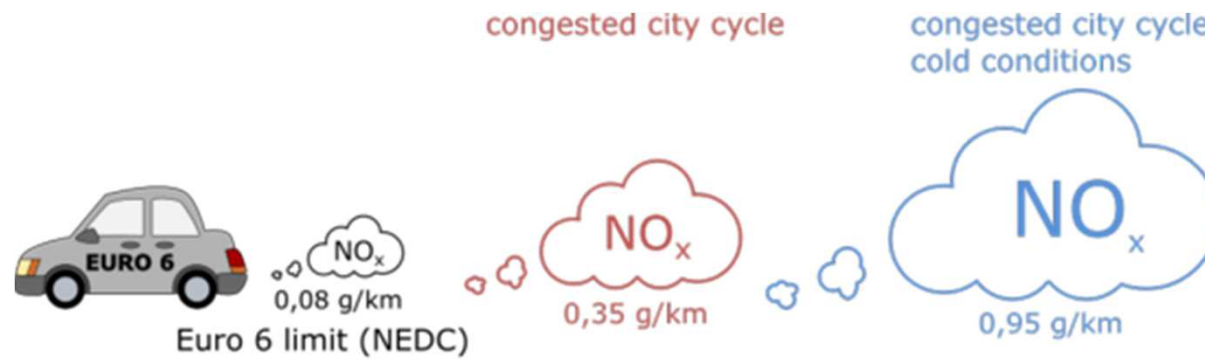
Problem: smog (smoke+fog) Shenzhen, China



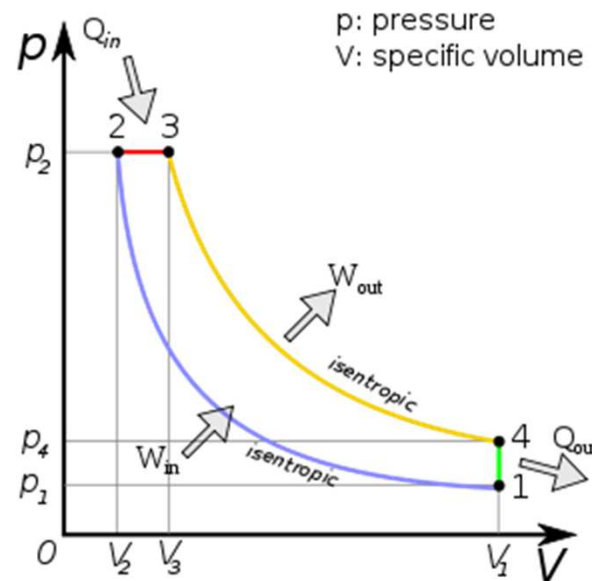
1st assignment: Flame Temperature Analysis and NOx Emissions for different Fuels and combustion conditions

Adiabatic flame temperature

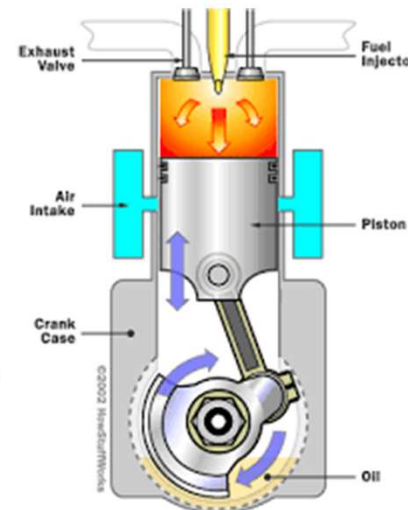
NOx emissions



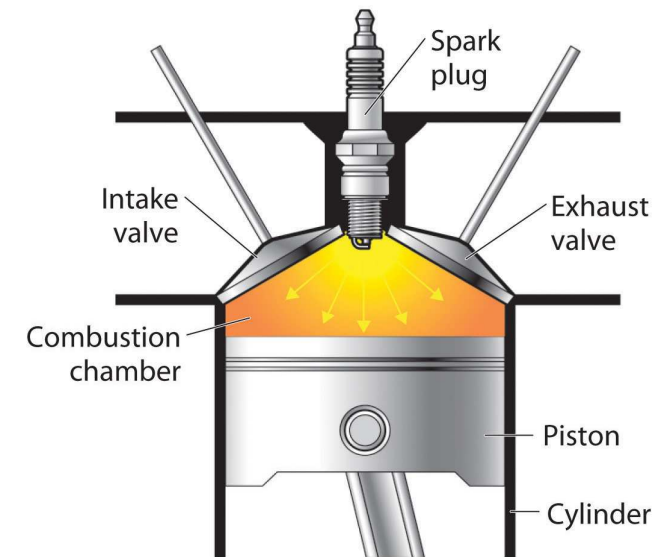
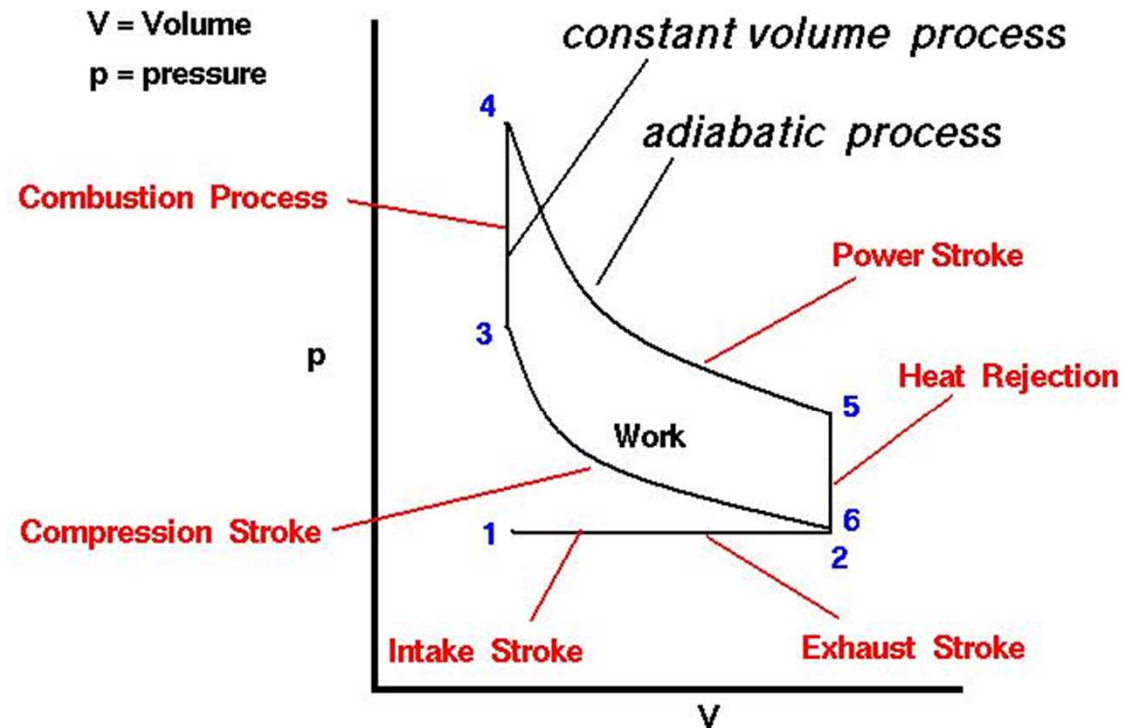
1st assignment: Flame Temperature Analysis and NOx Emissions for different Fuels and combustion conditions



Diesel theoretical P-v diagram
Q_{in} from combustion 2-3



1st assignment: Flame Temperature Analysis and NOx Emissions for different Fuels and combustion conditions



(a) Normal combustion

Gasoline theoretical P-v diagram
 Q_{in} from combustion 3-4

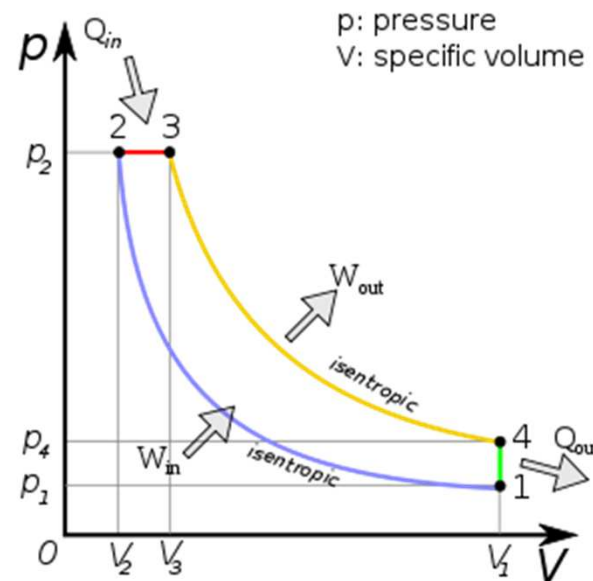
1st assignment: Flame Temperature Analysis and NOx Emissions for different Fuels and combustion conditions



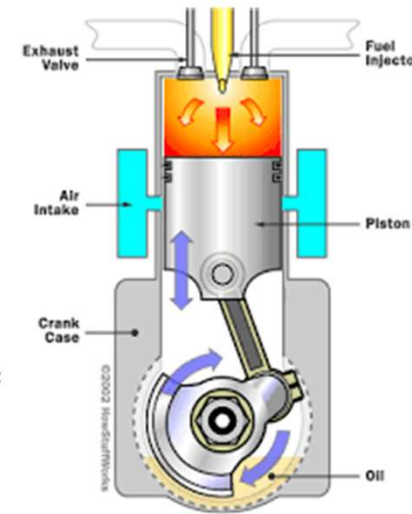
5 pages report+excel
spreadsheet with
calculations/matlab,
etc

P#9 Consider the combustion of C_7H_{14} (~diesel) with excess air $A/F = 40$. Determine the equilibrium composition of the product mixture:

- At 1200 K and 1 atm.
- At 1200 K and 10 atm.



Diesel theoretical P-v diagram
Q_{in} from combustion 2-3



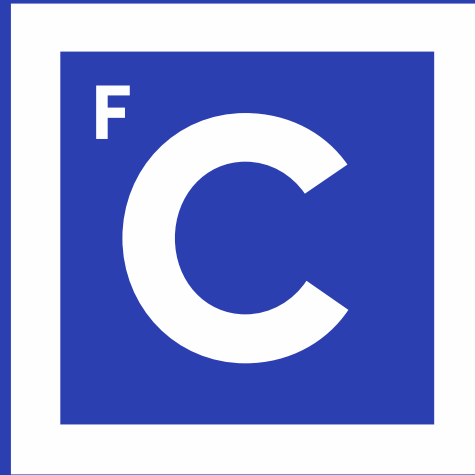
P#10 Following table list the results of an experiment of boiler that is used to produce superheated vapour. The boiler is feed by natural gas trough a conventional burner.

- 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 m³/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

The image consists of a large blue square. Inside this square is a white square, which is further enclosed by a smaller blue square. The word "Obrigado" is written in white, bold, sans-serif font in the center of the innermost blue square.

Obrigado



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de Ciências
da Universidade
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