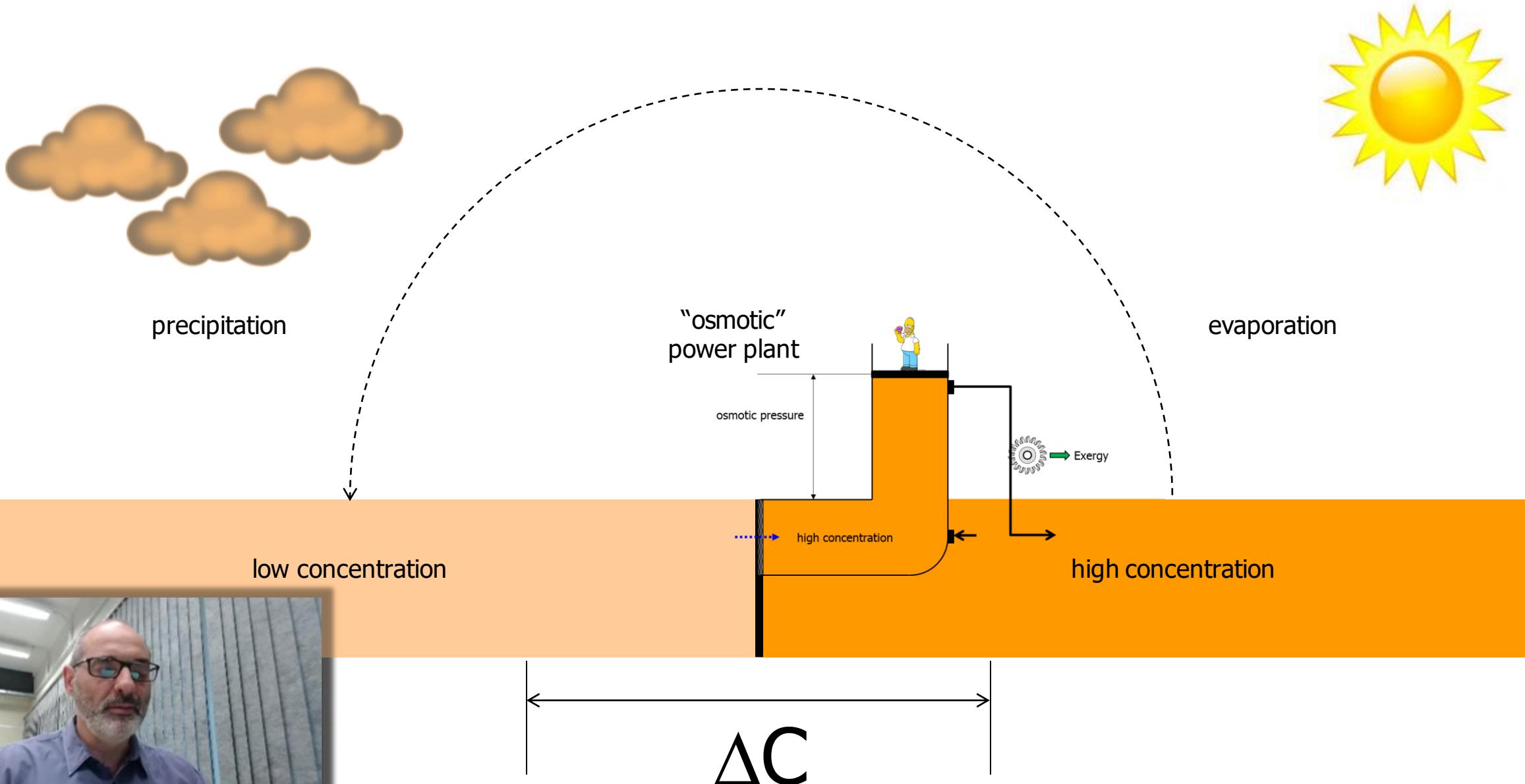


# EXERGY ANALYSIS: Gibbs free energy and chemical exergy

Prof. Paulo Seleg him Jr.  
Universidade de São Paulo



# Potential to generate work from differences in chemical composition



**agricultural system**

↑ Carbon



1500 EJ/yr

↓ Carbon  
**environment**

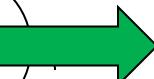
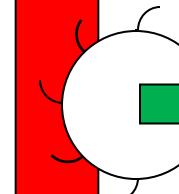
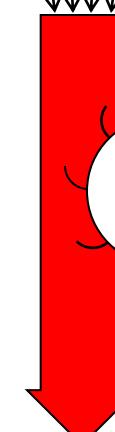
**agricultural system**

↑ Carbon



1500 EJ/yr

↓ Carbon  
**environment**



exergy

**agricultural system**

↑ Carbon



1500 EJ/yr



tedding

straw, cobs,  
etc.



bailing



**industrial system**

Chemical reactions for heat generation or for the conversion of biomass (feedstock) to energy carriers or chemical compounds...



preparation  
extraction, etc.

votor exergético  
"exergy carrier"



biochemical  
1G.

biochemical  
2G.

combustion  
pyrolysis, etc.

**carriers**

↓ Carbon  
environment

fuel

chemicals

fuel

chemicals

heat

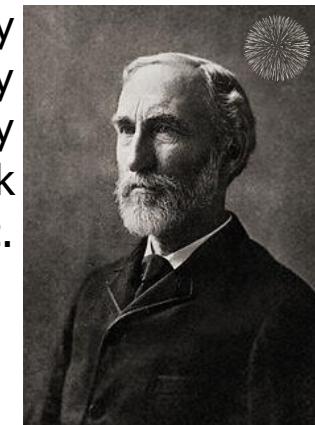
chemicals

electricity

→ exergy

# DEFINITIONS

Available energy  
Exergetic energy  
Availability  
Reversible work  
Etc.



## Exergy...

$$X \stackrel{\text{def}}{=} (U - U_0) + P_0(V - V_0) - T_0(S - S_0)$$

thermodynamic exergy

J. Willard Gibbs

$$X \stackrel{\text{def}}{=} (U - U_0) + P_0(V - V_0) - T_0(S - S_0) + EP + EC$$

thermodynamic exergy                                    mechanical exergy

$$X \stackrel{\text{def}}{=} (U - U_0) + P_0(V - V_0) - T_0(S - S_0) + EP + EC + EQ$$

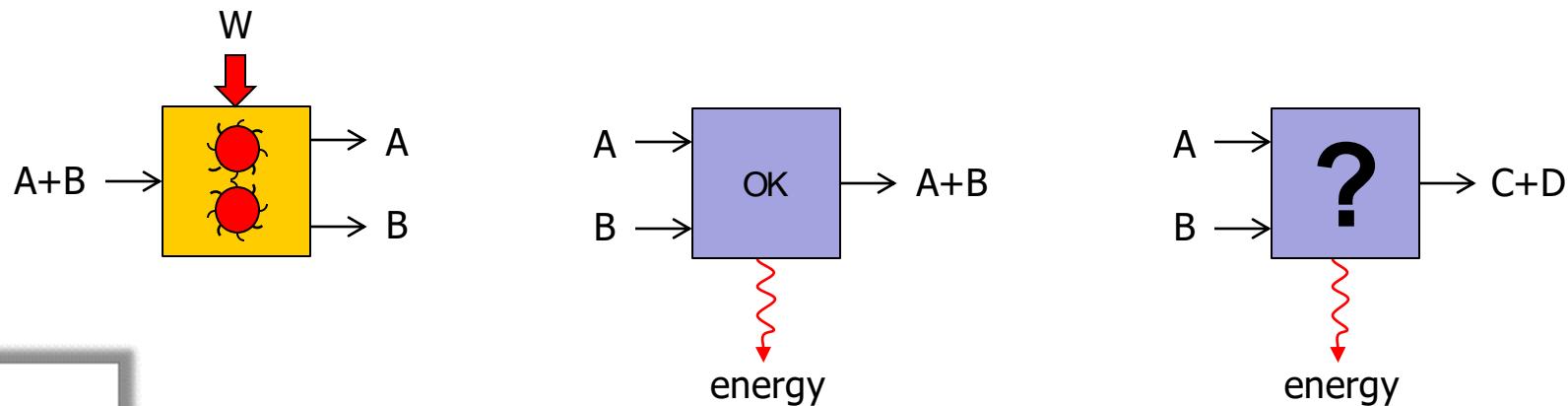
exergia termodinâmica                                    exergia mecânica                                    exergia química

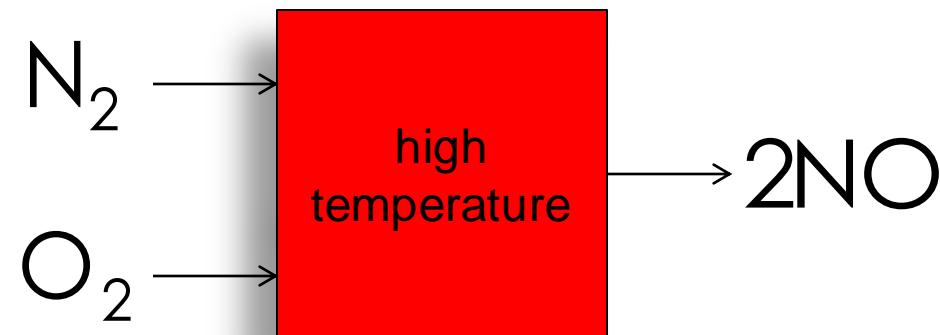
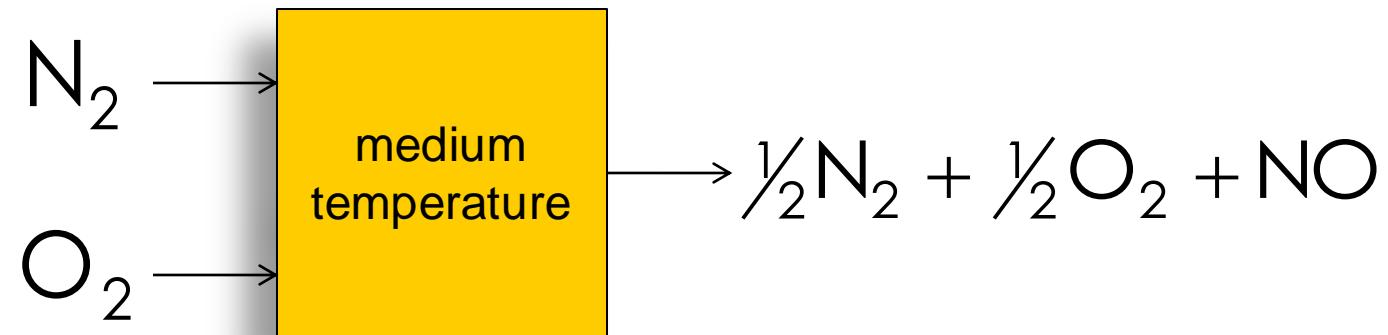
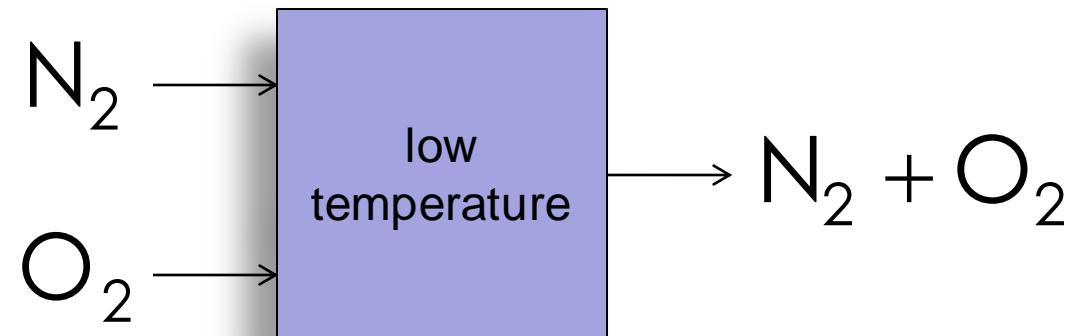
# **THERMODYNAMICS OF CHEMICAL REACTIONS:**

## Gibbs free energy and chemical exergy

# Entry point:

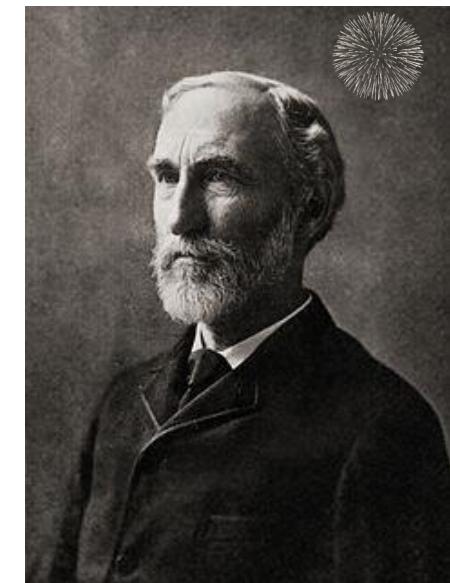
How to quantify the spontaneity of a bio,  
thermo or chemical process ?





# GIBBS FREE ENERGY:

Assessing the spontaneity of a process:  
thermodynamic potential that vanishes when  
the process reaches equilibrium at constant  
temperature and pressure ...



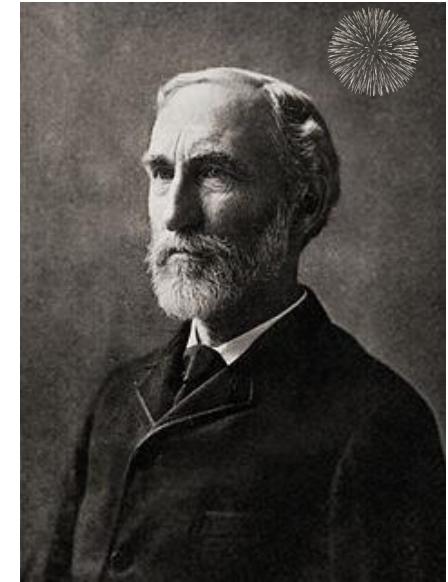
J. Willard Gibbs

# GIBBS FREE ENERGY:

Assessing the spontaneity of a process:  
thermodynamic potential that vanishes when  
the process reaches equilibrium at constant  
temperature and pressure ...

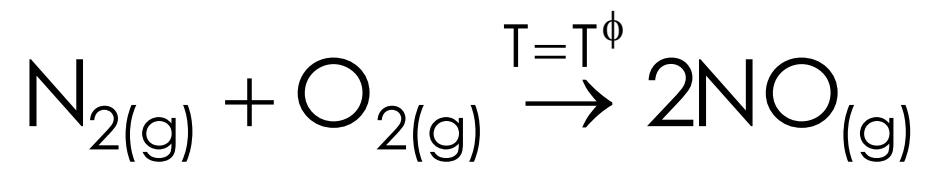
GIBBS FREE ENERGY →

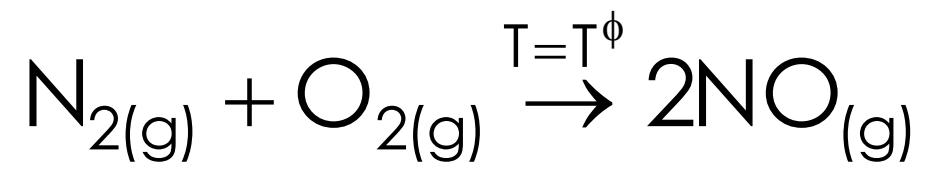
Gibbs free energy  
Gibbs function  
Gibbs potential  
Free enthalpy  
Etc.



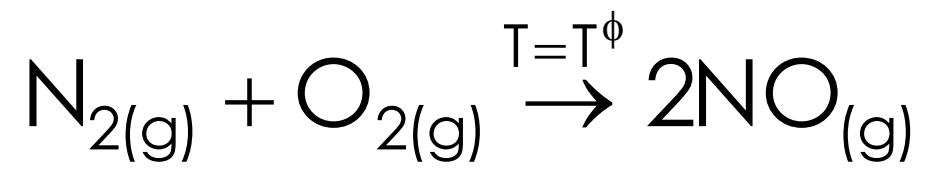
J. Willard Gibbs





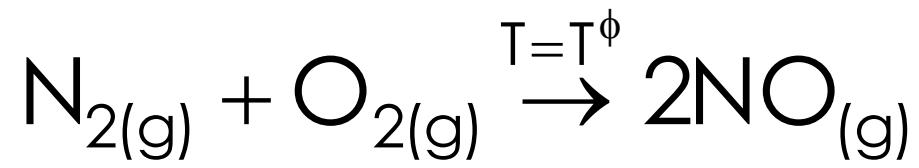


$$\Delta H = \sum_{\text{prod}} H_k(T) - \sum_{\text{reag}} H_k(T)$$



$$\Delta H = \sum_{\text{prod}} H_k(T) - \sum_{\text{reag}} H_k(T)$$

$$\Delta H = 2 \cdot \left( 90,29 \frac{\text{kJ}}{\text{mol}} \right) - 1 \cdot (0 + 0) = +180,58 \text{ kJ}$$



$$\Delta H = \sum_{\text{prod}} H_k(T) - \sum_{\text{reag}} H_k(T)$$

$$\Delta H = 2 \cdot \left( 90,29 \frac{\text{kJ}}{\text{mol}} \right) - 1 \cdot (0 + 0) = +180,58 \text{ kJ}$$

Endothermic

A energia necessária para a reação pode ser vir  
de uma fonte externa, ou da própria  
temperatura das moléculas...

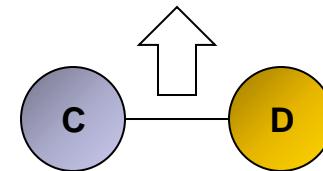
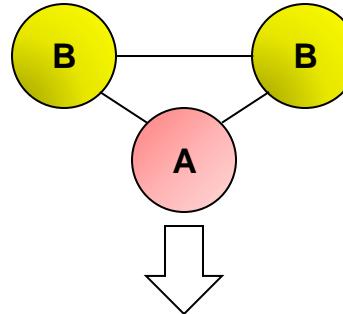
# CONJECTURES:

$\Delta H > 0$  (endothermic)  $\rightarrow$  “less” spontaneous

$\Delta H < 0$  (exothermic)  $\rightarrow$  “more” spontaneous

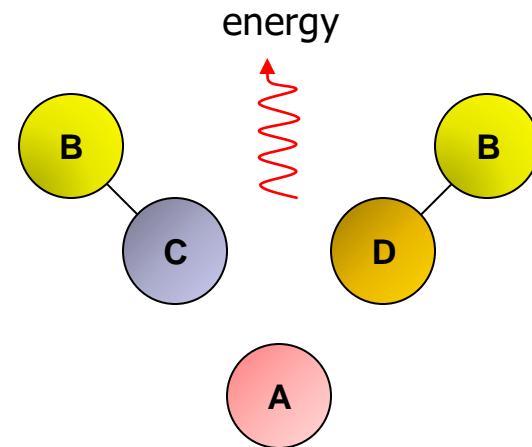
# Case 1: $\Delta H < 0$ e $\Delta S > 0$

greater  
quantity of  
microstates



# Case 1: $\Delta H < 0$ e $\Delta S > 0$

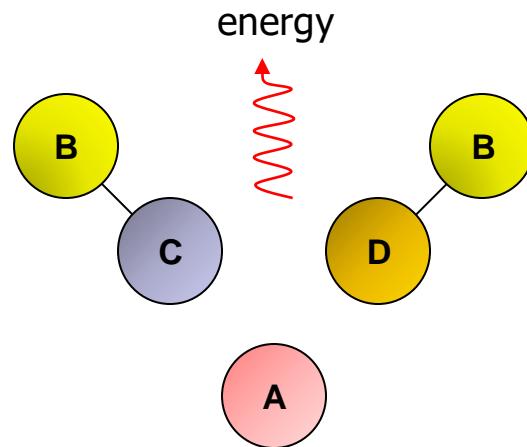
greater  
quantity of  
microstates



Crash test: two cars hitting each other and spreading various pieces...

# Case 1: $\Delta H < 0$ e $\Delta S > 0$

greater  
quantity of  
microstates



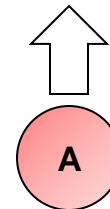
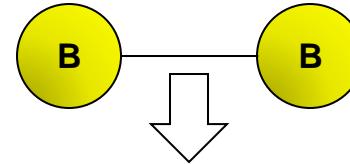
Crash test: two cars hitting each other and spreading various pieces...

Spontaneous in the indicated sense ( $\forall$  Temperature)

- Opposite sense → smaller probability of three molecules bumping into each other at the same time to form two molecules
- The products (three molecules) are at a lower energy level compared with the reagents ( $\Delta H < 0$ )

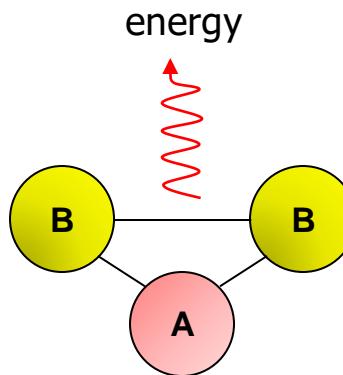
# Case 1: $\Delta H < 0$ e $\Delta S < 0$

**smaller**  
quantity of  
microstates



# Case 1: $\Delta H < 0$ e $\Delta S < 0$

**smaller**  
quantity of  
microstates



"Inverse" crash test:  
many parts bumping  
into each other  
assembling a car...

Conditionally spontaneous in the indicated direction

- Low temperature: favors spontaneity (greater and better contact time for the parts to assemble in the correct way...)
- High temperature: hinders spontaneity (contact time is too short and kinetic energy is too high...)

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder		
$\Delta S < 0$ less disorder		

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	?	
$\Delta S < 0$ less disorder		

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	
$\Delta S < 0$ less disorder		

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	
$\Delta S < 0$ less disorder		?

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	
$\Delta S < 0$ less disorder		non spontaneous

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	?
$\Delta S < 0$ less disorder		non spontaneous

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder		non spontaneous

# Spontaneity Table

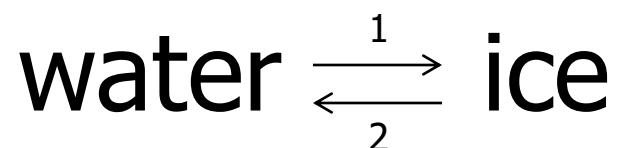
	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	?	non spontaneous

# Spontaneity Table

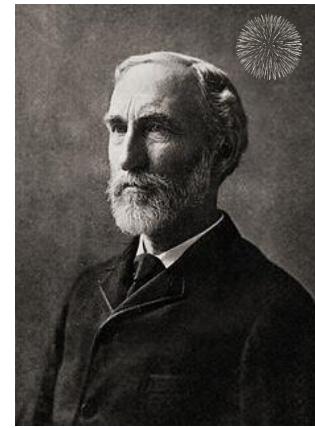
	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous

# Spontaneity Table

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous



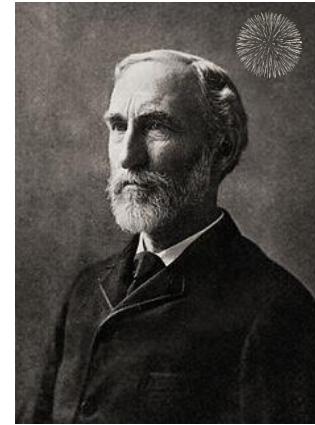
$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$



J. Willard Gibbs

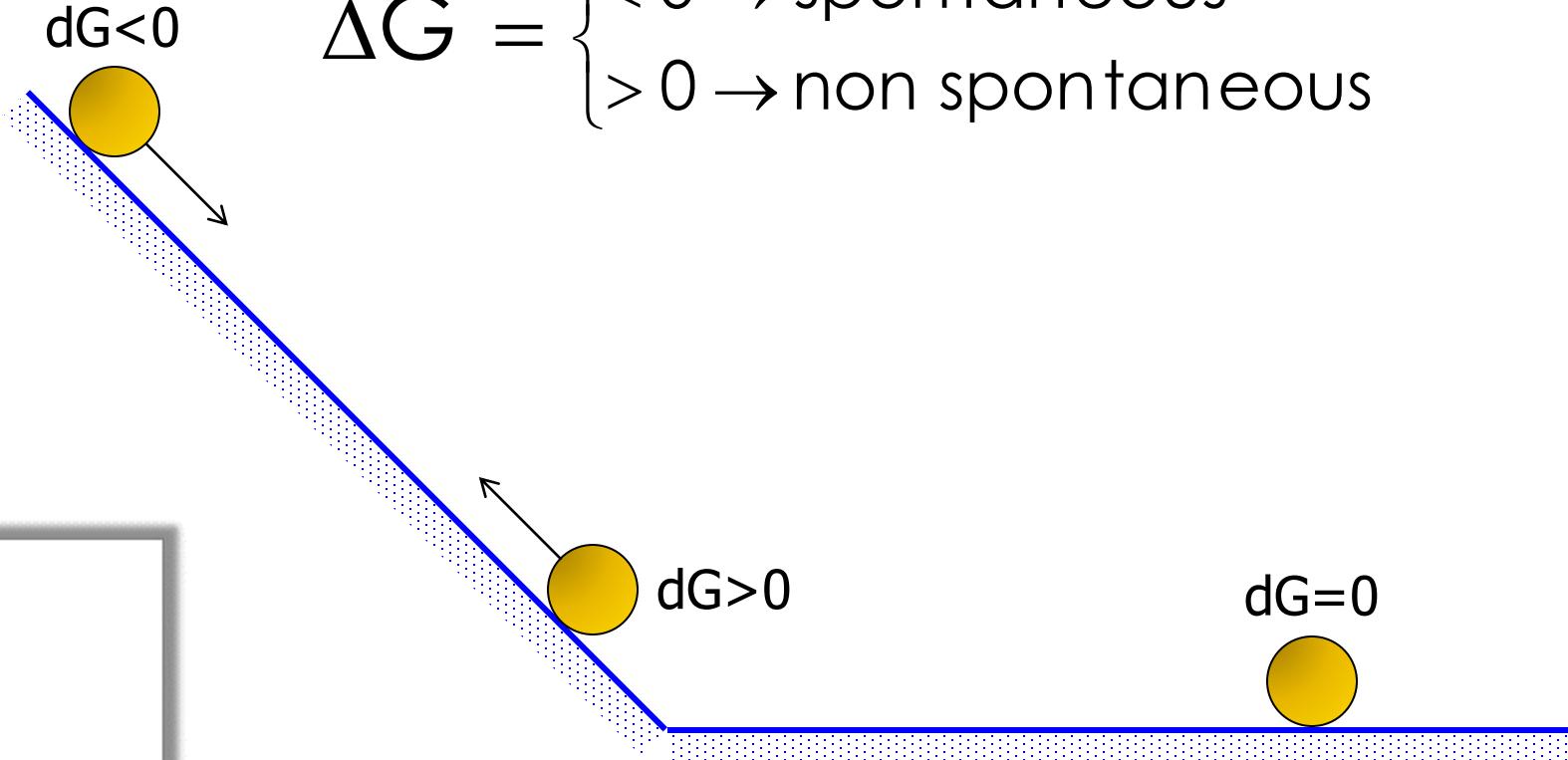
A measure of a processes' spontaneity:  
thermodynamic potential that vanishes when  
the system reaches equilibrium  
at constant pressure and temperature...

$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$

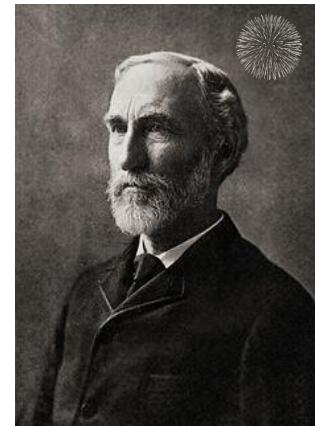


J. Willard Gibbs

$$\Delta G \stackrel{\text{def}}{=} \begin{cases} < 0 \rightarrow \text{spontaneous} \\ > 0 \rightarrow \text{non spontaneous} \end{cases}$$



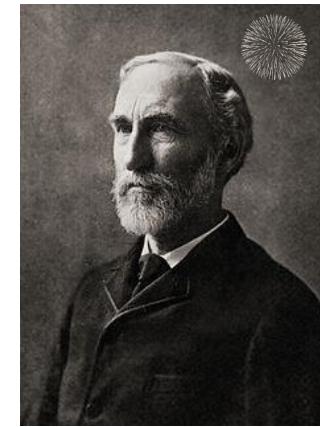
$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$



J. Willard Gibbs

$$\Delta G \stackrel{\text{def}}{=} \begin{cases} < 0 \rightarrow \text{spontaneous} \\ > 0 \rightarrow \text{non spontaneous} \end{cases}$$

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous

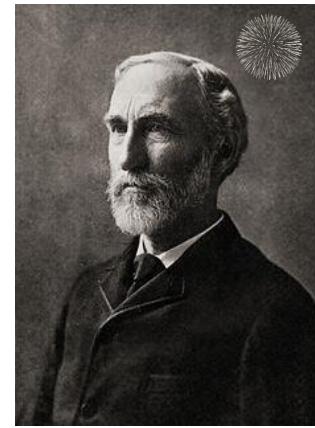


$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$

J. Willard Gibbs

$$\Delta G^{\text{prop}} = +\Delta H - \dots \Delta S \quad \leftarrow \text{different physical units}$$

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous

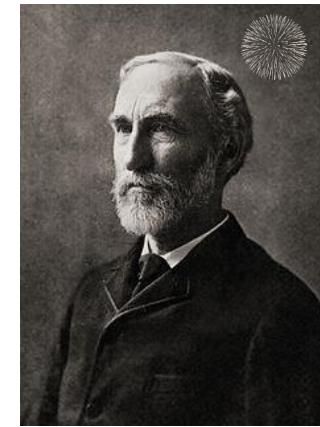


$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$

J. Willard Gibbs

$$\Delta G^{\text{prop}} = +\Delta H + \dots - T \cdot \Delta S$$

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous

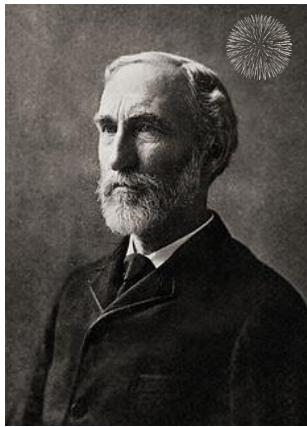


$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$

J. Willard Gibbs

$$\Delta G \stackrel{\text{def}}{=} \Delta H - T \cdot \Delta S$$

	$\Delta H < 0$ exothermic	$\Delta H > 0$ endothermic
$\Delta S > 0$ more disorder	spontaneous	spontaneous at high temperatures
$\Delta S < 0$ less disorder	spontaneous at low temperatures	non spontaneous

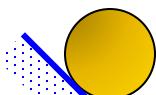


J. Willard Gibbs

$$\Delta G^{\text{prop}} = A(\Delta H) + B(T, \Delta S)$$

$$G \stackrel{\text{def}}{=} H - T \cdot S$$

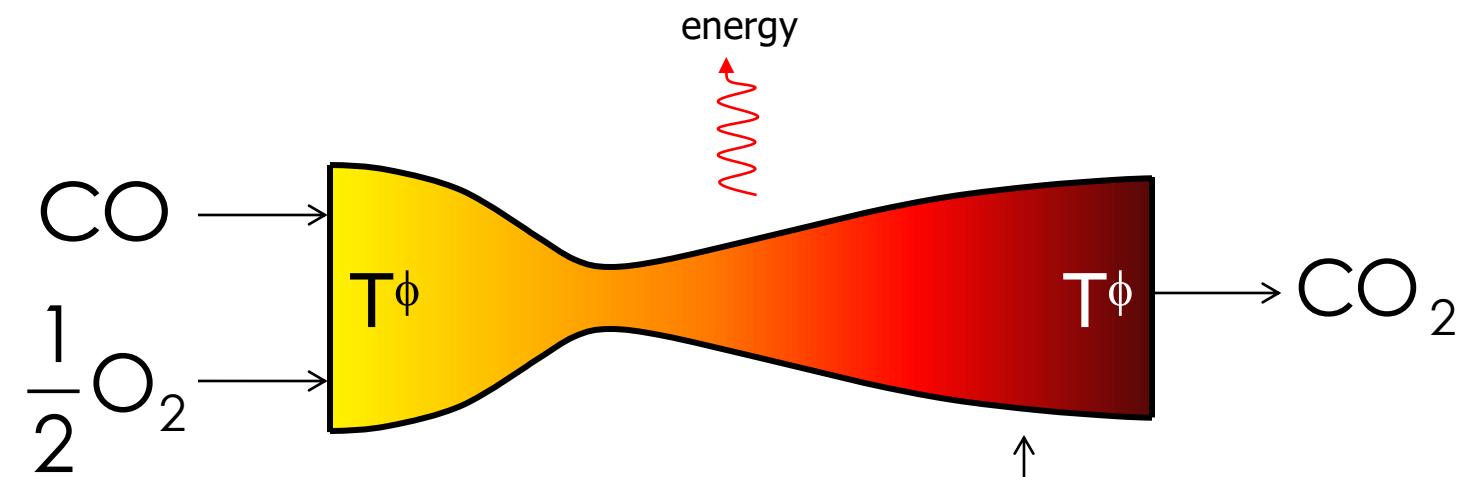
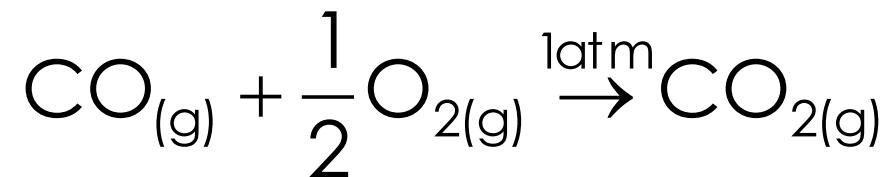
$dG < 0$



# Practical application:

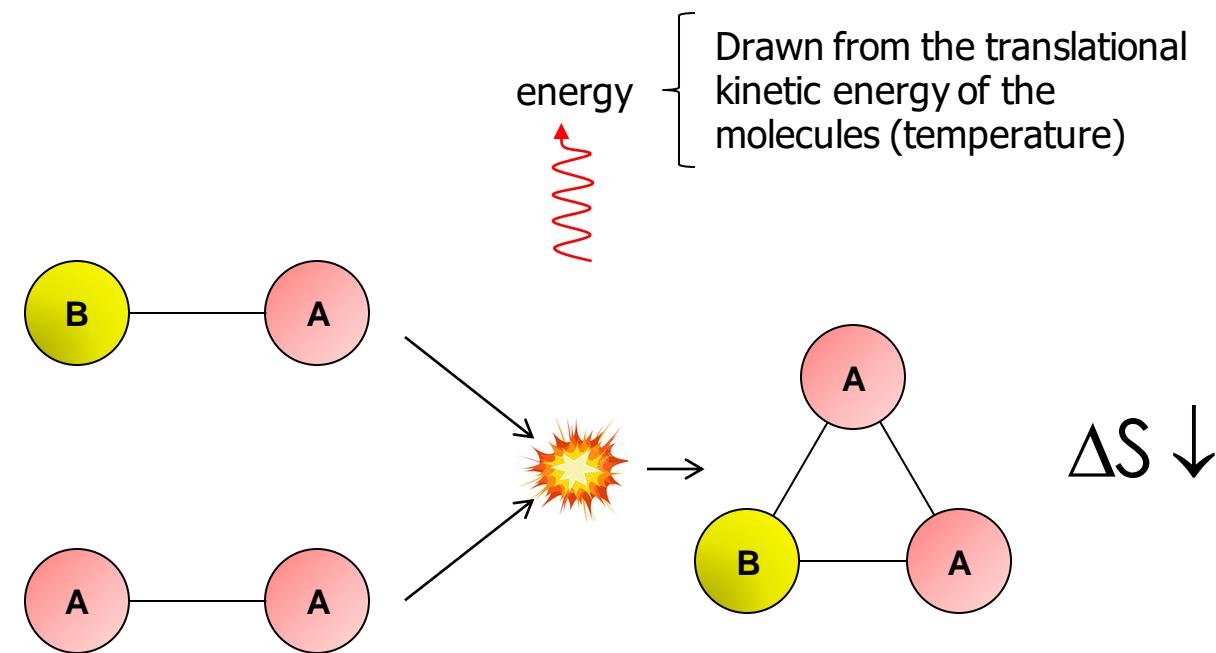
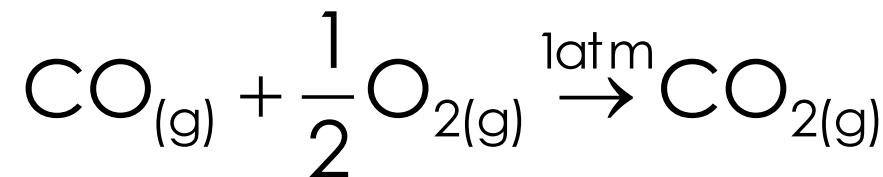


Example: spontaneity analysis of carbon monoxide oxidation in function of the temperature



The energy content of the combustion products is inferior to the reagents

# Example: spontaneity analysis of carbon monoxide oxidation in function of the temperature



Oxidation occurring @  $T^\phi$  ( $25^\circ\text{C} = 298\text{K}$ )

$$\Delta G \stackrel{\text{def}}{=} \Delta H - T \cdot \Delta S$$

$$\Delta H^\phi = \sum_{\text{prod}} n_k \Delta h_{f,k}^\phi - \sum_{\text{reag}} n_k \Delta h_{f,k}^\phi$$

$$\Delta S^\phi = \sum_{\text{prod}} n_k \Delta s_{f,k}^\phi - \sum_{\text{reag}} n_k \Delta s_{f,k}^\phi$$

## Charted data...

$$\Delta h_{f,CO}^\phi = -110,53 \text{ kJ/mol}$$

$$\Delta s_{f,CO}^\phi = 197,67 \text{ J/mol/K}$$

$$\Delta h_{f,O_2}^\phi = 0$$

$$\Delta s_{f,O_2}^\phi = 205,14 \text{ J/mol/K}$$

$$\Delta h_{f,CO_2}^\phi = -393,51 \text{ kJ/mol}$$

$$\Delta s_{f,CO_2}^\phi = 213,74 \text{ J/mol/K}$$

$$C_{P,CO} = 29,14 \text{ J/mol}$$

$$C_{P,O_2} = 29,38 \text{ J/mol}$$

$$C_{P,CO_2} = 37,11 \text{ J/mol}$$

$$\Delta H^\phi = \sum_{\text{prod}} n_k \Delta h_{f,k}^\phi - \sum_{\text{reag}} n_k \Delta h_{f,k}^\phi$$

$$\Delta H^\phi = [1 \cdot (-393,51)] - [1 \cdot (-110,53) + 1/2 \cdot (0)]$$

$$\Delta H^\phi = -282,98 \text{ kJ}$$

---

$$\Delta S^\phi = \sum_{\text{prod}} n_k \Delta s_{f,k}^\phi - \sum_{\text{reag}} n_k \Delta s_{f,k}^\phi$$

$$\Delta S^\phi = [1 \cdot (213,74)] - [1 \cdot (197,67) + 1/2 \cdot (205,14)]$$

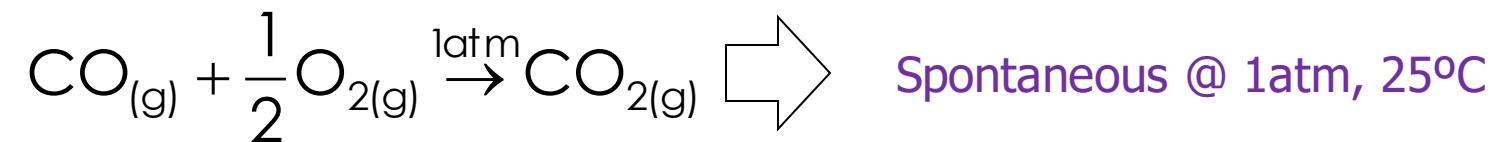
$$\Delta S^\phi = -86,5 \frac{\text{J}}{\text{K}}$$

$$\Delta G^\phi = \Delta H^\phi - T \cdot \Delta S^\phi$$

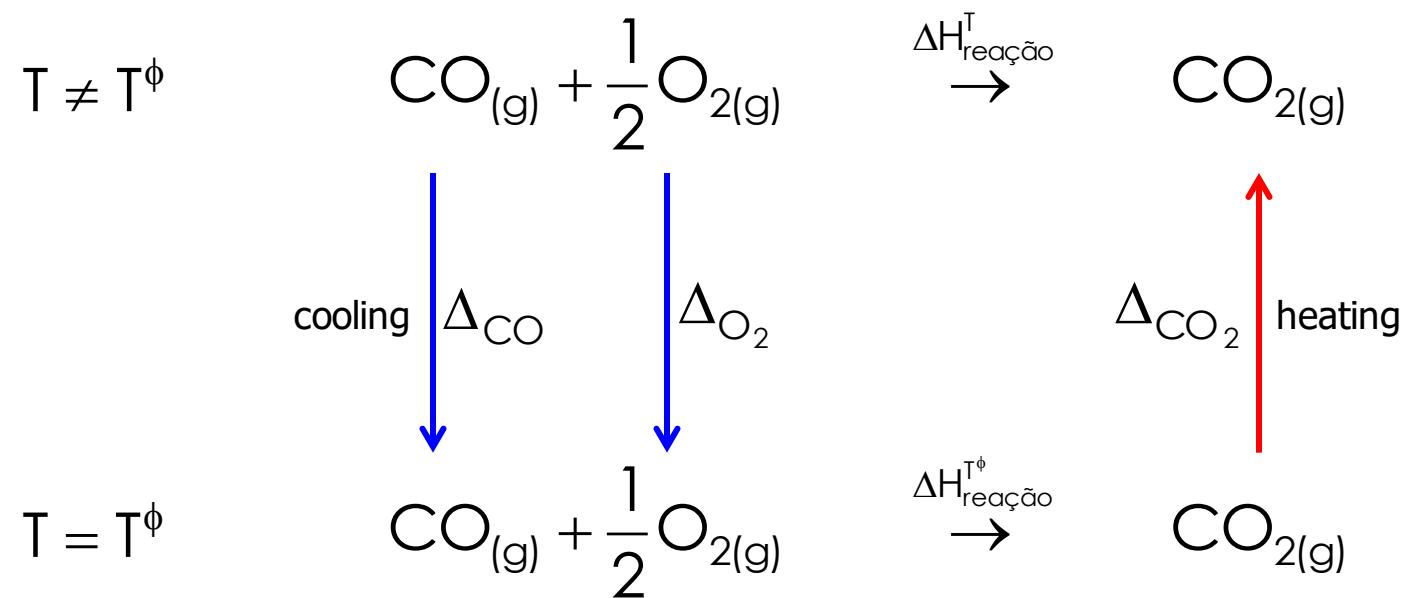
$$\Delta H^\phi = -282,98 \text{ kJ} \quad \Delta S^\phi = -86,5 \frac{\text{kJ}}{\text{K}}$$

$$\Delta G^\phi = -282,98 \text{ kJ} - 298\text{K} \cdot (-86,5 \cdot 10^{-3} \text{ kJ/K})$$

$$\Delta G^\phi = -257,203 \text{ kJ}$$

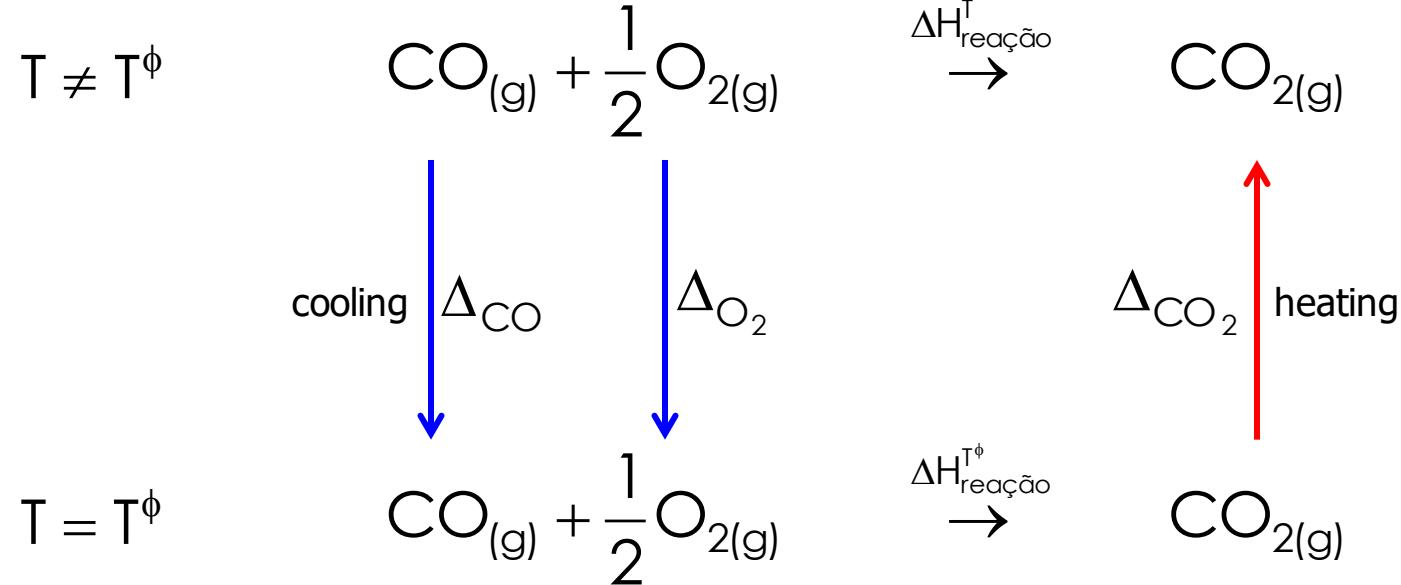


# Oxidation occurring @ $T \neq T^\phi$ (Hess law)



$$\Delta H_{\text{reac}}^T = \Delta_{\text{CO}} + \Delta_{\text{O}_2} + \Delta H_{\text{reac}}^{T^\phi} + \Delta_{\text{CO}_2}$$

# Oxidation occurring @ $T \neq T^\phi$ (Hess law)



$$\Delta_k = \pm n_k \int_{T^\phi}^T C_{P,k} \cdot dT$$

$$\Delta_k = \pm n_k C_{P,k} \cdot (T - T^\phi)$$

## Oxidation occurring @ $T \neq T^\phi$ (Hess law)

$$\Delta_k = \pm n_k C_{P,k} \cdot (T - T^\phi)$$

$$C_{P,CO} = 29,14 \text{ J/mol} \quad \Delta_{CO} = -1 \cdot 29,14 \cdot (T - 298) = -29,14 \cdot (T - 298)$$

$$C_{P,O_2} = 29,38 \text{ J/mol} \quad \Delta_{O_2} = -1/2 \cdot 29,38 \cdot (T - 298) = -14,69 \cdot (T - 298)$$

$$C_{P,CO_2} = 37,11 \text{ J/mol} \quad \Delta_{CO_2} = +1 \cdot 37,11 \cdot (T - 298) = +37,11 \cdot (T - 298)$$

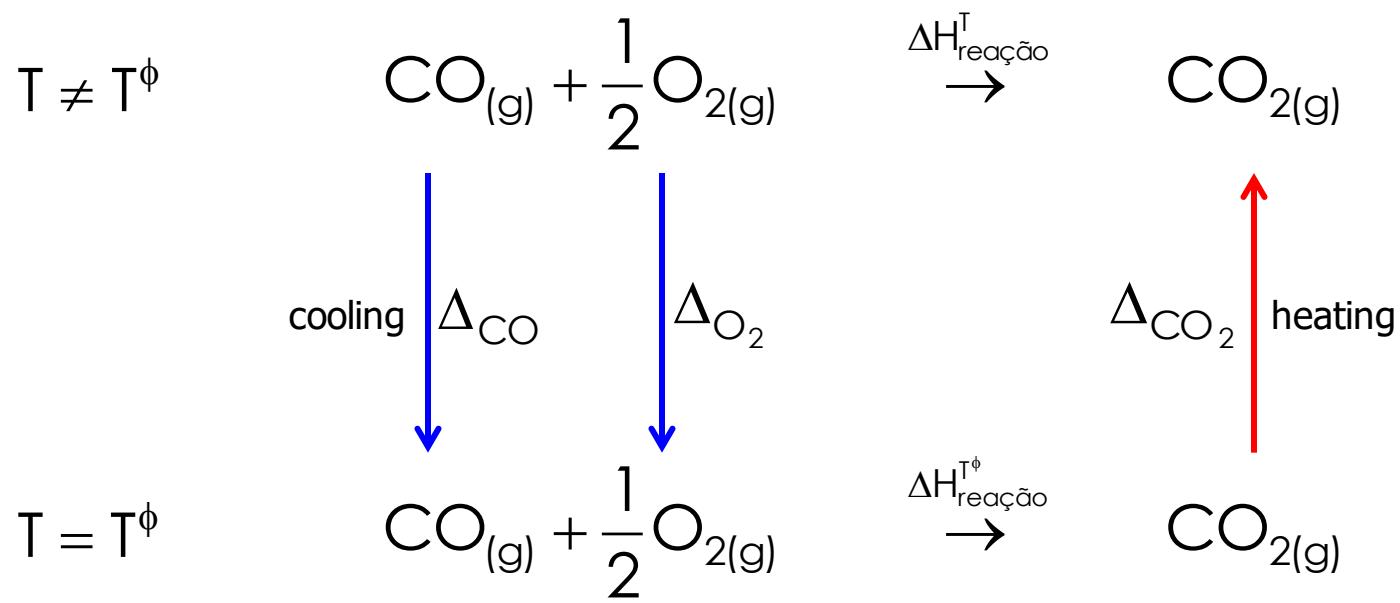
---

$$\Delta H_{\text{reac}}^T = \Delta_{CO} + \Delta_{O_2} + \Delta H_{\text{reac}}^{T^\phi} + \Delta_{CO_2}$$

$$\Delta H_{\text{reac}}^T = (-29,14 - 14,69 + 37,11) \cdot 10^{-3} \cdot (T - 298) - 282,98$$

$$\Delta H_{\text{reac}}^T = -280,98 - 6,72 \cdot 10^{-3} \cdot T$$

# Oxidation occurring @ $T \neq T^\phi$ (Hess law)



$$\Delta_k = \pm n_k \int_{T^\phi}^T \frac{C_{P,k}}{T} \cdot dT \quad \text{Obs.: } P_k = \text{cte}$$

$$\Delta_k = \pm n_k C_{P,k} \cdot \ln(T/T^\phi)$$

## Oxidation occurring @ $T \neq T^\phi$ (Hess law)

$$\Delta_k = \pm n_k C_{P,k} \cdot \ln(T/T^\phi)$$

$$C_{P,CO} = 29,14 \text{ J/mol} \quad \Delta_{CO} = -1 \cdot 29,14 \cdot \ln(T/298) = -29,14 \cdot \ln(T/298)$$

$$C_{P,O_2} = 29,38 \text{ J/mol} \quad \Delta_{O_2} = -1/2 \cdot 29,38 \cdot \ln(T/298) = -14,69 \cdot \ln(T/298)$$

$$C_{P,CO_2} = 37,11 \text{ J/mol} \quad \Delta_{CO_2} = +1 \cdot 37,11 \cdot \ln(T/298) = +37,11 \cdot \ln(T/298)$$

---

$$\Delta S_{\text{reac}}^T = \Delta_{CO} + \Delta_{O_2} + \Delta S_{\text{reac}}^{T^\phi} + \Delta_{CO_2}$$

$$\Delta S_{\text{reac}}^T = (-29,14 - 14,69 + 37,11) \cdot \ln(T/298) - 86,5$$

$$\Delta S_{\text{reac}}^T = -86,5 - 6,72 \cdot \ln(T/298)$$

## Oxidation occurring @ $T \neq T^\phi$ (Hess law)

$$\Delta H_{\text{reac}}^T = -280,98 - 6,72 \cdot 10^{-3} \cdot T \quad [\Delta H_{\text{reac}}^T] = \text{kJ}$$

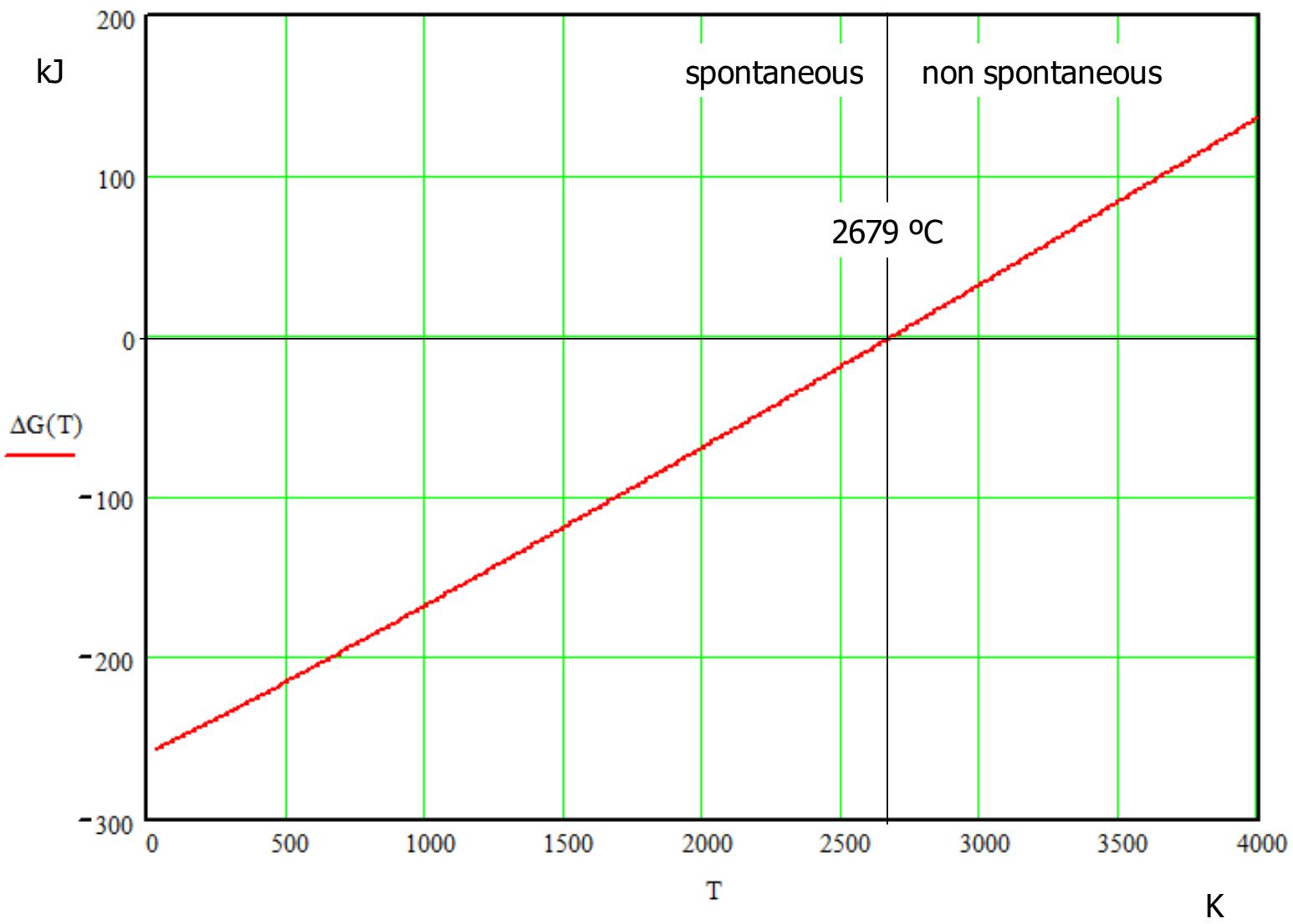
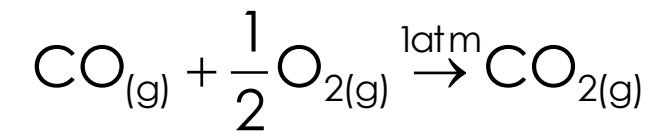
$$\Delta S_{\text{reac}}^T = -86,5 - 6,72 \cdot \ln(T/298) \quad [\Delta S_{\text{reac}}^T] = \text{J}$$

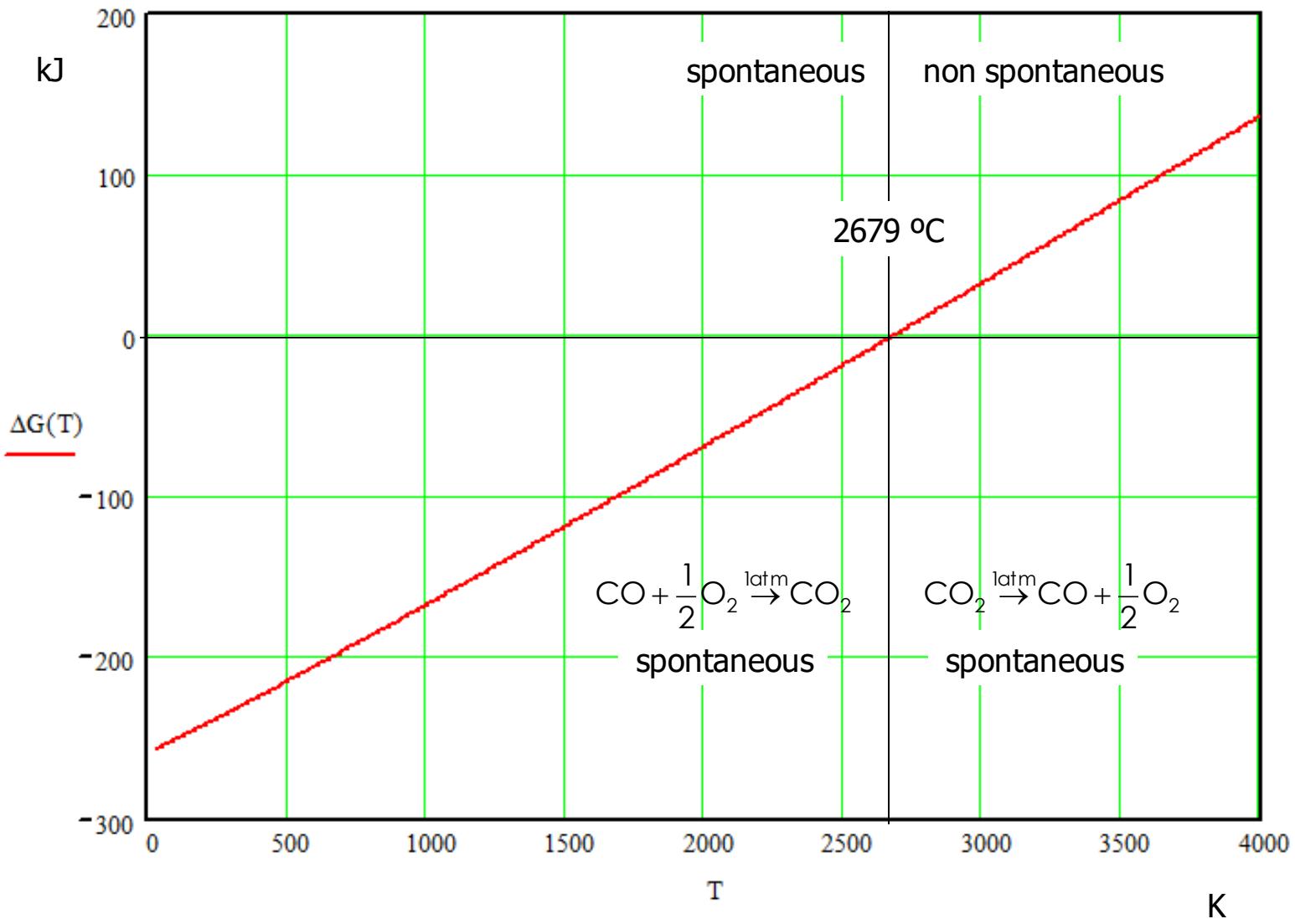
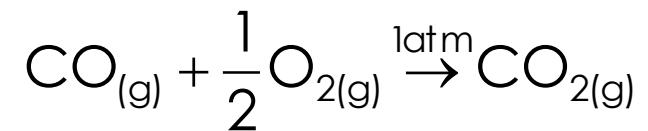
$$\Delta G^\phi = \Delta H^\phi - T \cdot \Delta S^\phi$$

$$\Delta G_{\text{reac}}^T = -280,98 - 6,72 \cdot 10^{-3} \cdot T - T \cdot [-86,5 - 6,72 \cdot \ln(T/298)] \cdot 10^{-3}$$

---

$$\Delta G_{\text{reac}}^T = -280,98 + T \cdot [79,78 + 6,72 \cdot \ln(T/298)] \cdot 10^{-3}$$





# CHEMICAL EXERGY



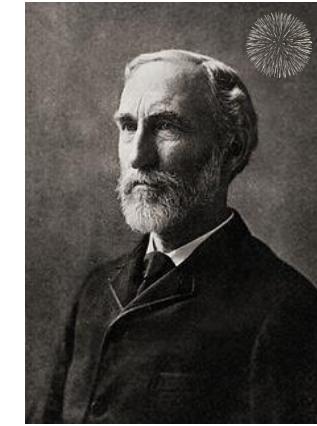


The capacity of generating useful mechanical work (exergy) is a COMBINED environment/system property...

$$X^{\text{def}} = \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}} + EP + EC + \boxed{EQ} \underbrace{\quad}_{\text{chemical exergy}}$$

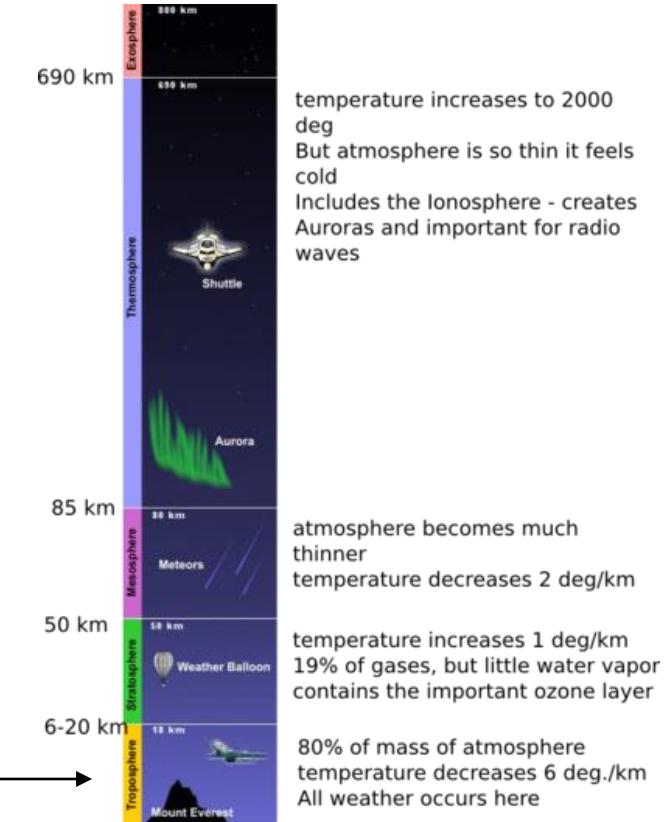
# Chemical exergy:

the maximum quantity of useful mechanical work that can be obtained from a system when it chemically transforms itself until chemical equilibrium is established with the environment...



J. Willard Gibbs

Gas		Volume <sup>(A)</sup>	
Name	Formula	in ppmv <sup>(B)</sup>	in %
Nitrogen	N <sub>2</sub>	780,840	78.084
Oxygen	O <sub>2</sub>	209,460	20.946
Argon	Ar	9,340	0.9340
Carbon dioxide	CO <sub>2</sub>	397	0.0397
Neon	Ne	18.18	0.001818
Helium	He	5.24	0.000524
Methane	CH <sub>4</sub>	1.79	0.000179



# **Standard Chemical Exergy of Atmospheric Gases:**

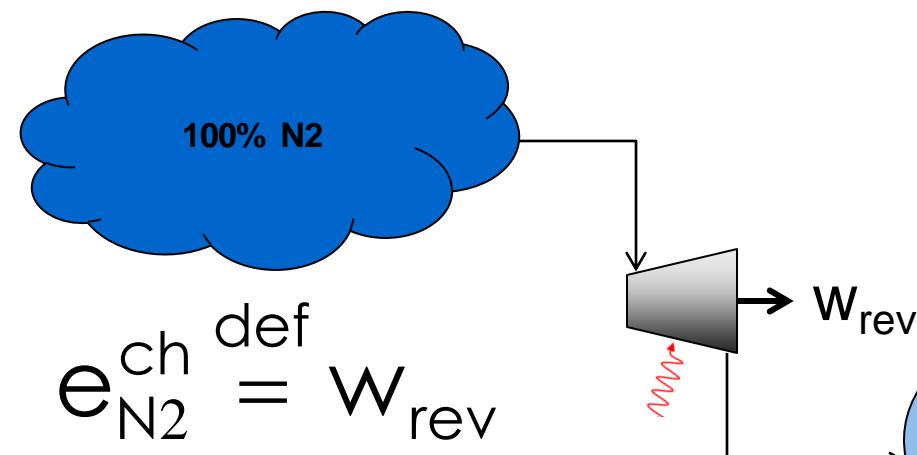
Bringing earth's atmosphere to its pre industrial revolution composition

# Recovering the pre industrial revolution atmosphere



# Standard Chemical Exergy of Atmospheric Gases

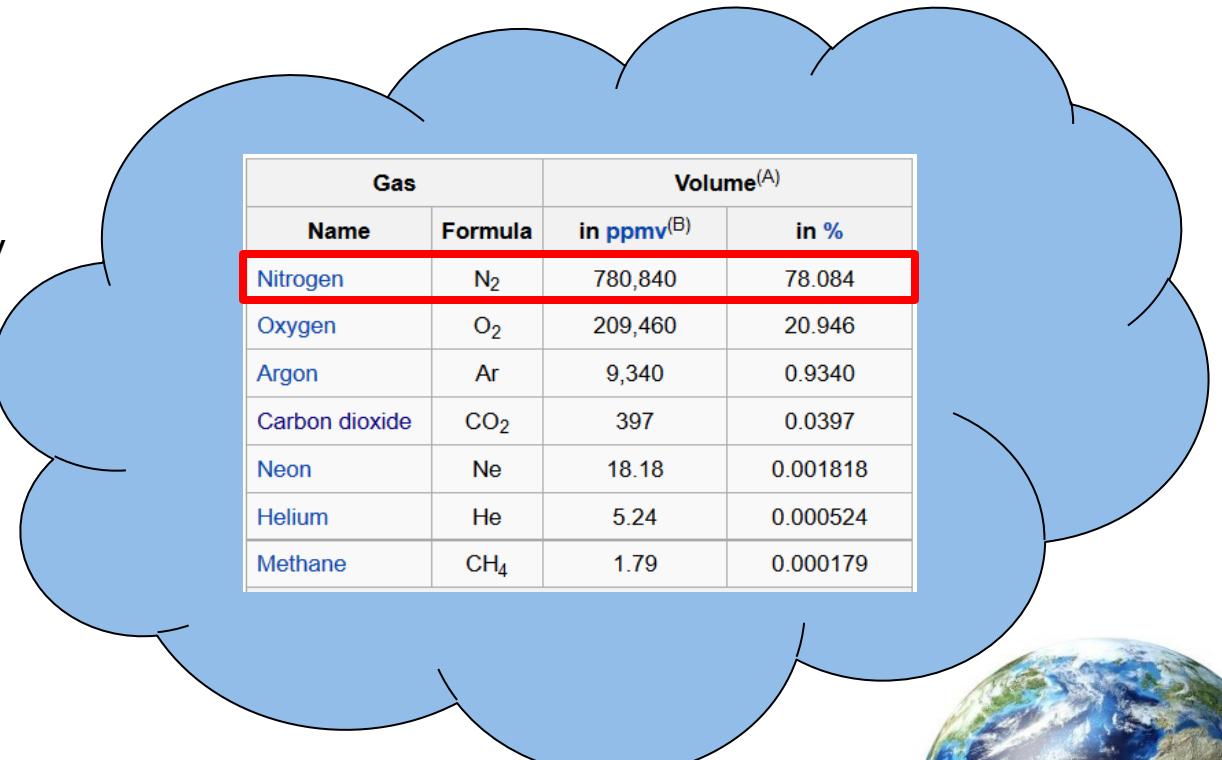
$$P_{N_2} = 1 \text{ bar}, T_{N_2} = 25^\circ\text{C}$$



Reversible expansion work  
from  $P_0$  to  $P_{N_2}$  @  $T=T_0$  (cte)

$$W_{rev} = -RT_0 \cdot \ln(P_{N_2}^e / P_0)$$

$$P_0 = 1 \text{ bar}, T_0 = 25^\circ\text{C}$$
$$P_{N_2} = x_{N_2}^e \cdot P_0$$



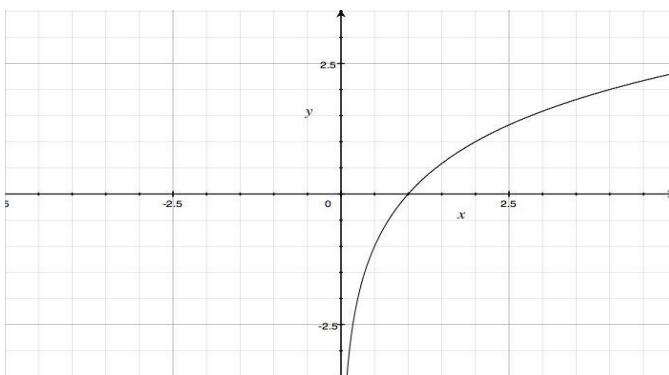
$$W_{rev} = -RT_0 \cdot \ln(x_{N_2}^e)$$



# Standard Chemical Exergy of Atmospheric Gases

atmosfera = “estado morto”

Gas		Volume <sup>(A)</sup>	
Name	Formula	in ppmv <sup>(B)</sup>	in %
Nitrogen	N <sub>2</sub>	780,840	78.084
Oxygen	O <sub>2</sub>	209,460	20.946
Argon	Ar	9,340	0.9340
Carbon dioxide	CO <sub>2</sub>	397	0.0397
Neon	Ne	18.18	0.001818
Helium	He	5.24	0.000524
Methane	CH <sub>4</sub>	1.79	0.000179



$$e_{N_2}^{ch} = -RT_0 \cdot \ln(x_{N_2}^e) = \dots$$

$$\dots = -8.314 \frac{J}{molK} \cdot (25 + 273.1)K \cdot \ln(0.781)$$

$$e_{N_2}^{ch} = 613.2 J/mol$$

$$e_{O_2}^{ch} = -RT_0 \cdot \ln(x_{O_2}^e) = \dots$$

$$\dots = -8.314 \frac{J}{molK} \cdot (25 + 273.1)K \cdot \ln(0.2095)$$

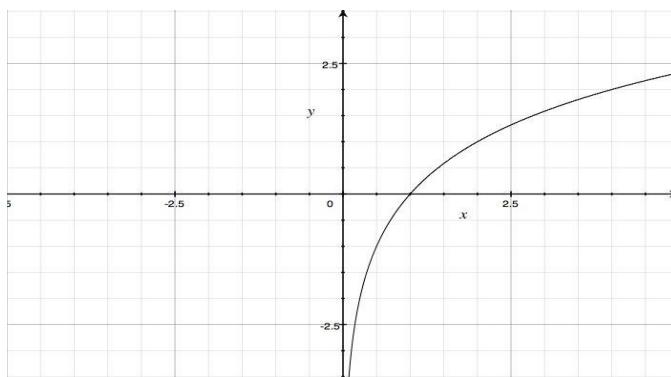
$$e_{O_2}^{ch} = 3874.9 J/mol$$

Extracting O<sub>2</sub> from the atmosphere requires more exergy than extracting N<sub>2</sub> because its molar concentration is smaller

# Standard Chemical Exergy of Atmospheric Gases

atmosfera = "estado morto"

Gas		Volume <sup>(A)</sup>	
Name	Formula	in ppmv <sup>(B)</sup>	in %
Nitrogen	N <sub>2</sub>	780,840	78.084
Oxygen	O <sub>2</sub>	209,460	20.946
Argon	Ar	9,340	0.9340
Carbon dioxide	CO <sub>2</sub>	397	0.0397
Neon	Ne	18.18	0.001818
Helium	He	5.24	0.000524
Methane	CH <sub>4</sub>	1.79	0.000179



$$e_{\text{Ar}}^{\text{ch}} = -RT_0 \cdot \ln(x_{\text{Ar}}^e) = \dots$$

$$\dots = -8.314 \frac{\text{J}}{\text{molK}} \cdot (25 + 273.1)\text{K} \cdot \ln(0.00934)$$

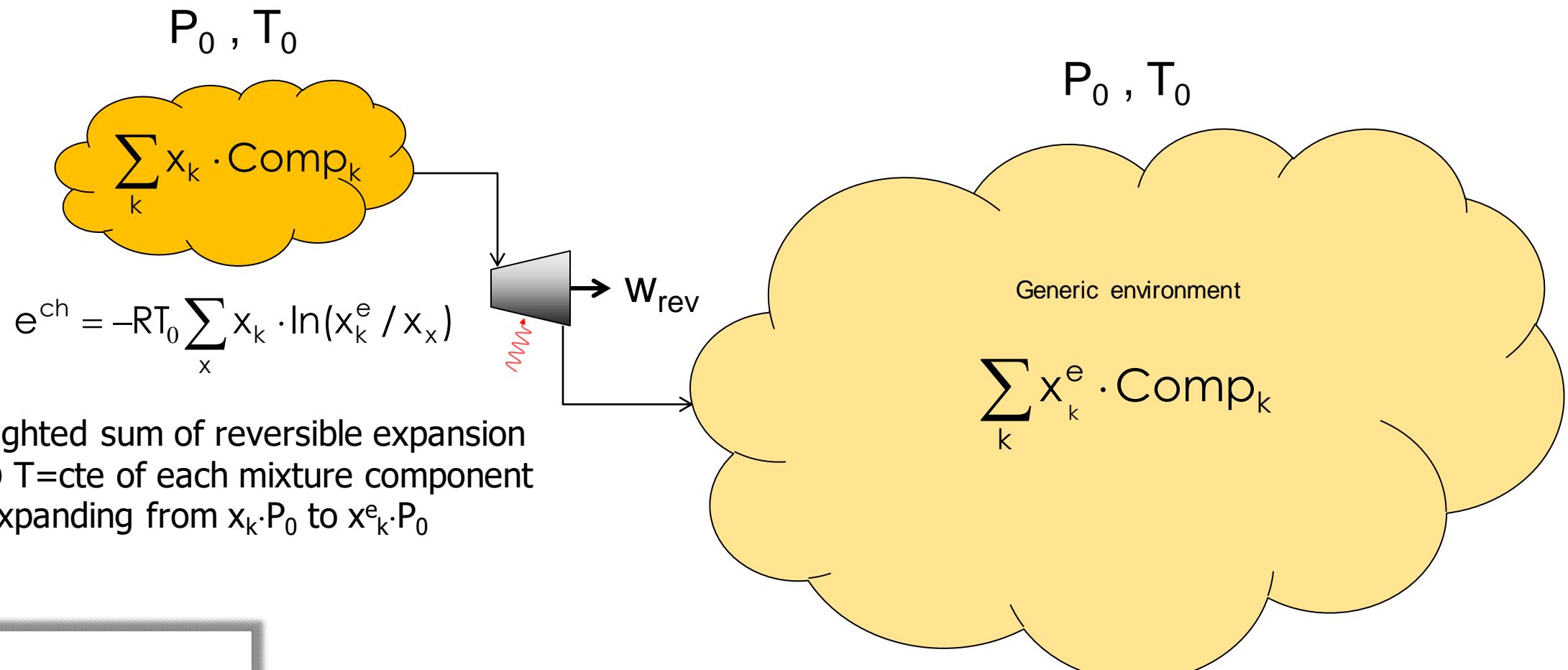
$$e_{\text{Ar}}^{\text{ch}} = 11584.6 \text{ J/mol}$$

$$e_{\text{CO}_2}^{\text{ch}} = -RT_0 \cdot \ln(x_{\text{CO}_2}^e) = \dots$$

$$\dots = -8.314 \frac{\text{J}}{\text{molK}} \cdot (25 + 273.1)\text{K} \cdot \ln(0.000397)$$

$$e_{\text{CO}_2}^{\text{ch}} = 19413.0 \text{ J/mol}$$

# Standard Chemical Exergy of a Mixture of Environmental Gases



$$e^{\text{ch}} = -RT_0 \sum_x x_k \cdot (\ln x_k^e - \ln x_k) = \dots$$

Compositional differences enable  
the production of work...

# Standard Chemical Exergy of a Mixture of Environmental Gases

$$e^{ch} = -RT_0 \sum_x x_k \cdot (\ln x_k^e - \ln x_k) = \dots$$

$$\downarrow e_k^{ch} = -RT_0 \cdot \ln(x_k^e)$$

$$e^{ch} = \sum_x x_k \cdot e_k^{ch} + RT_0 \sum_x x_k \cdot \ln x_k$$

Chemical exergy based on  
a model environment

Molar concentration defines a “chemical  
distance” to the environment

$$x_k = x_k^e \quad \forall k \Rightarrow e^{ch} = 0$$

# Standard Chemical Exergy of a Mixture of Environmental Gases

$$e^{ch} = -RT_0 \sum_x x_k \cdot (\ln x_k^e - \ln x_k) = \dots$$

$$\downarrow e_k^{ch} = -RT_0 \cdot \ln(x_k^e)$$

$$e^{ch} = \sum_x x_k \cdot e_k^{ch} + RT_0 \sum_x x_k \cdot \ln x_k$$

Chemical exergy based on  
a model environment

Molar concentration defines a “chemical  
distance” to the environment

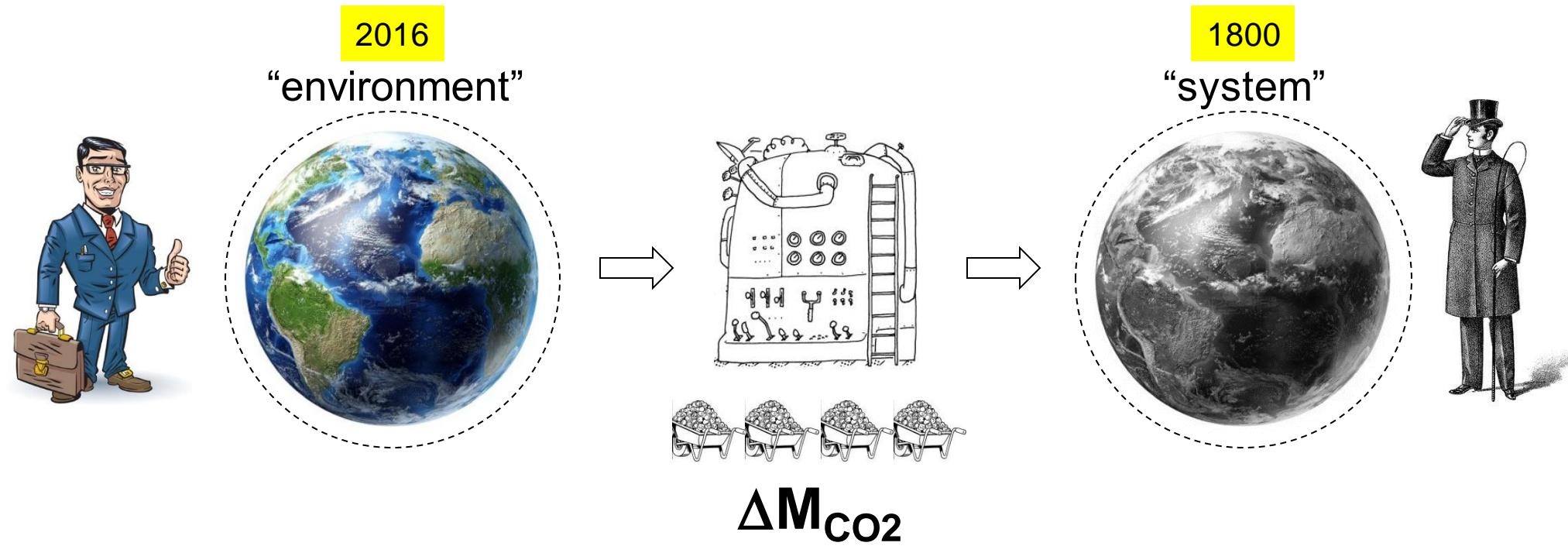
$$x_k = x_k^e \quad \forall k \Rightarrow e^{ch} = 0$$

Chemical exergy can also be defined as the minimum amount of mechanical work necessary to reconstitute the state and composition of a system from the environment through compression, chemical reaction, etc.

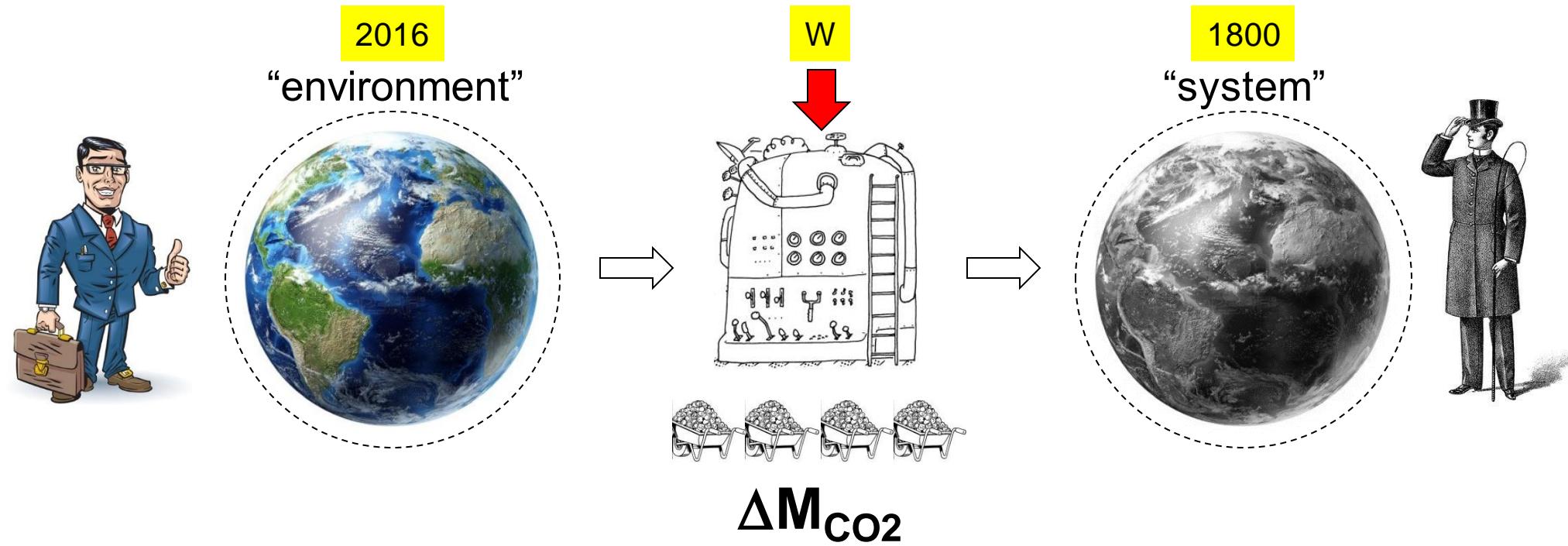
# Recovering the pre industrial revolution atmosphere



# Recovering the pre industrial revolution atmosphere

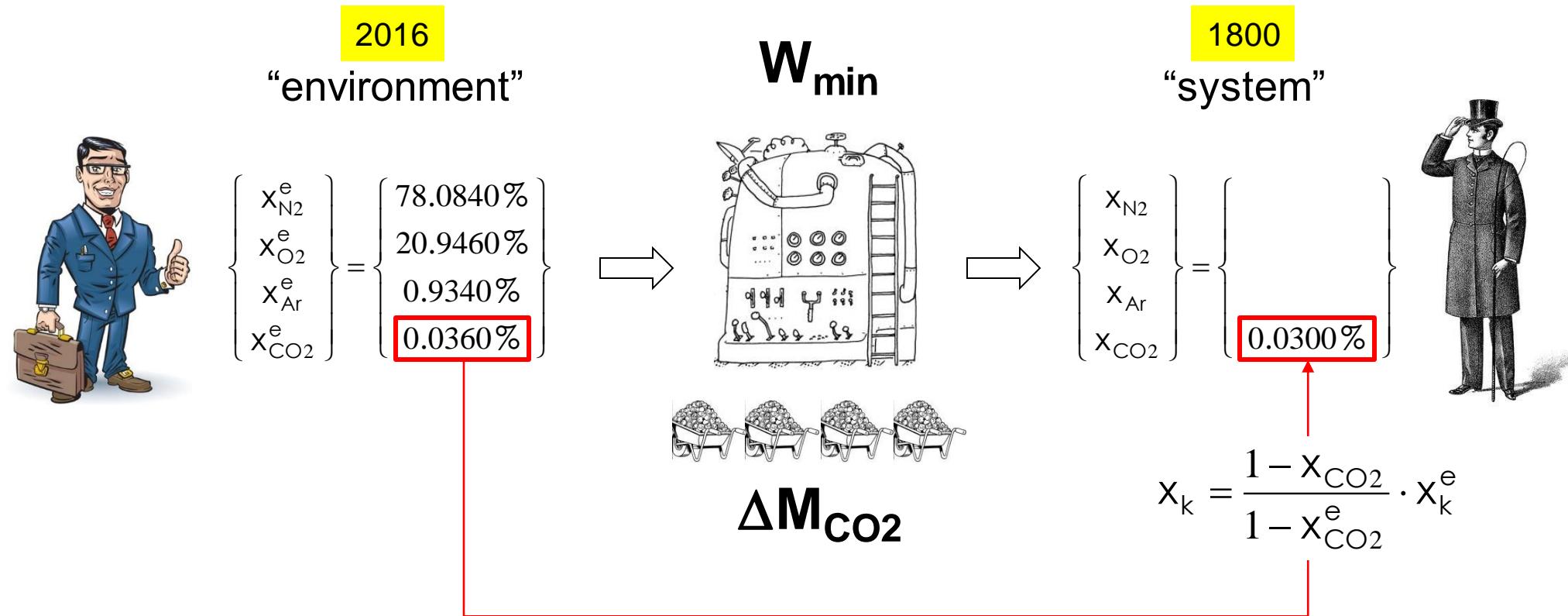


# Recovering the pre industrial revolution atmosphere



But is it feasible ? What is the minimum amount of exergy necessary to remove CO<sub>2</sub> from the atmosphere so that its concentration drops to levels prior to the industrial revolution ?

# Recovering the pre industrial revolution atmosphere



$$W_{min} = -RT_0 \sum_x x_k \cdot (\ln x_k^e - \ln x_k) = \dots$$

# Recovering the pre industrial revolution atmosphere

$$w_{\min} = -RT_0 \sum_x x_k \cdot (\ln x_k^e - \ln x_k) = \dots$$

$$w_{\min} = -8.314(25 + 273.15)[0.780887(\ln(0.78040) - (\ln(0.78088)) + 0.209473\dots]$$

universal  
gas constant

$$w_{\min} = -0.01315 \text{ J/mol}$$

total mas of earth's  
atmosphere

$$W_{\min} = -0.01315 \frac{\text{J}}{\text{mol}} \times \frac{1}{28.97 \text{ g/mol}} \times 5.1480 \times 10^{18} \text{ kg}$$

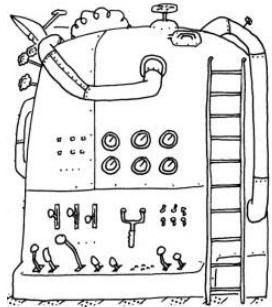
molar mas of  
atmospheric air

$$W_{\min} = -2.337 \times 10^{18} \text{ J}$$

$$W_{\text{world}} \approx 78.4 \times 10^{18} \text{ J} \sim \text{eleven days !}$$

(world power consumption)

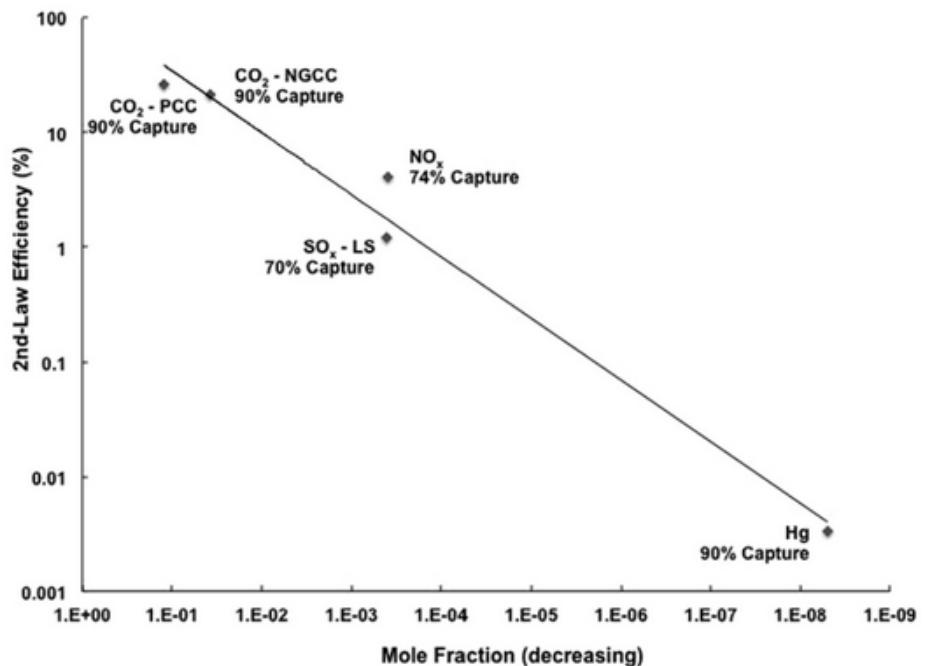
$$W_{\text{real}} \geq W_{\text{min}}$$



$$\Delta M_{\text{CO}_2}$$

### 1.6 Cost of CO<sub>2</sub> Capture

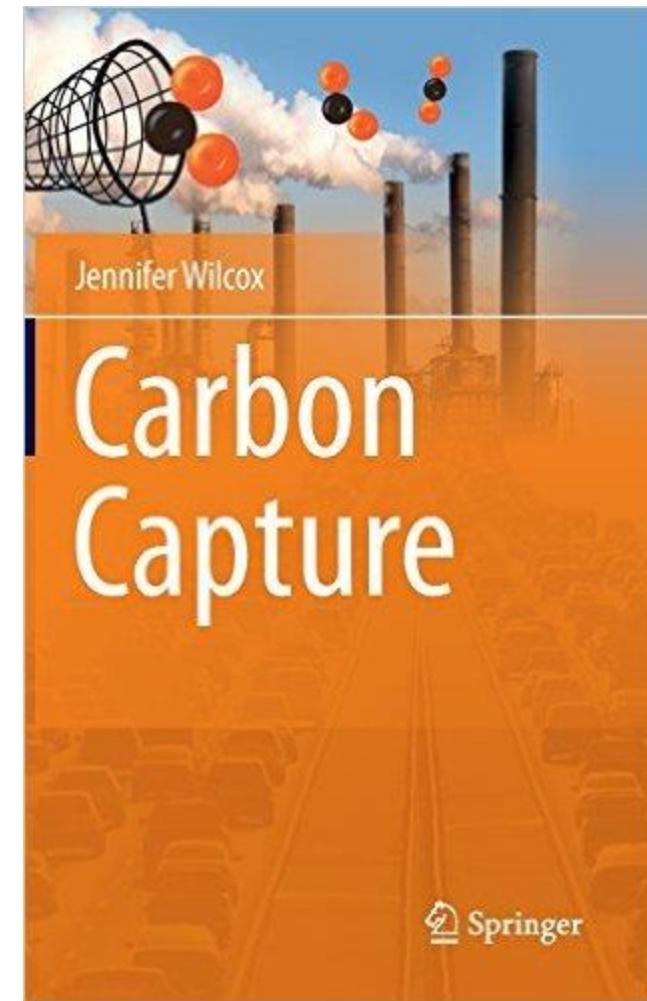
27



**Fig. 1.12** Plot showing the relationship between the 2nd-law efficiency and concentration of initial gas mixture

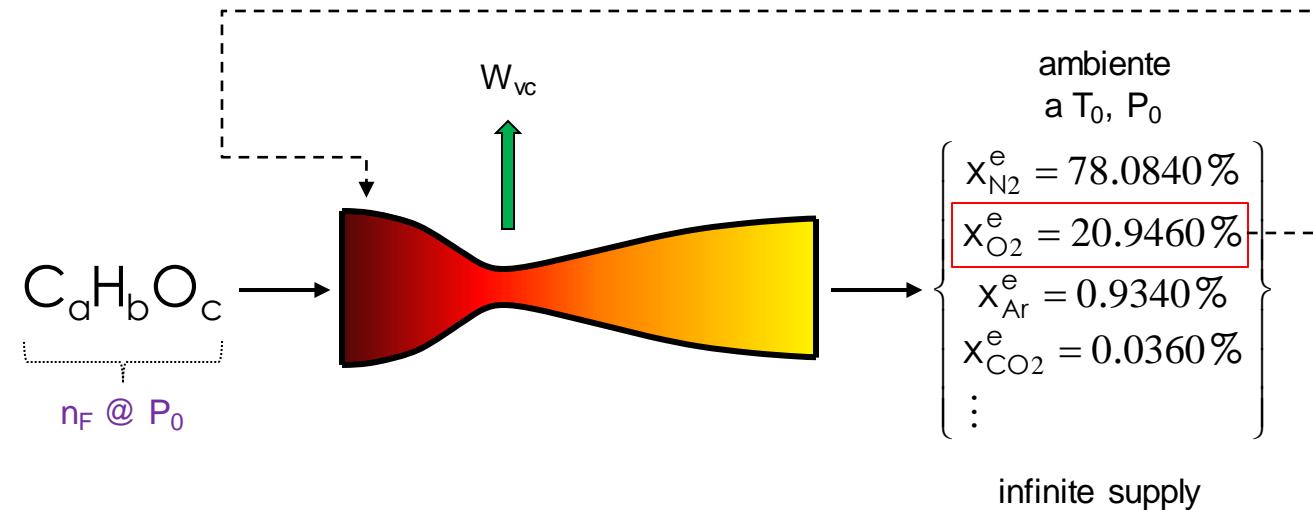
that low-sulfur Appalachian bituminous coal was burned in a 500-MW utility boiler. The capture technologies assumed for CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, and Hg consisted of amine scrubbing, wet flue gas desulfurization, selective catalytic reduction, and activated carbon injection, respectively. In the case of NGCC, precombustion separation based upon amine scrubbing is assumed for a 477-MW plant. It is interesting to note that the 2nd-law efficiency decreases with decreasing CO<sub>2</sub> concentration [48]. This implies that there are still efficiencies to gain in SO<sub>x</sub>, NO<sub>x</sub>, and Hg capture since these processes do not include regeneration, yet they still follow the trend.

48. House KZ, Baclig AC, Ranjan M, van Nierop EA, Wilcox J, Herzog HJ (2011) Economic and energetic analysis of capturing CO<sub>2</sub> from ambient air. Proc Natl Acad Sci USA 108(51):20428–20433



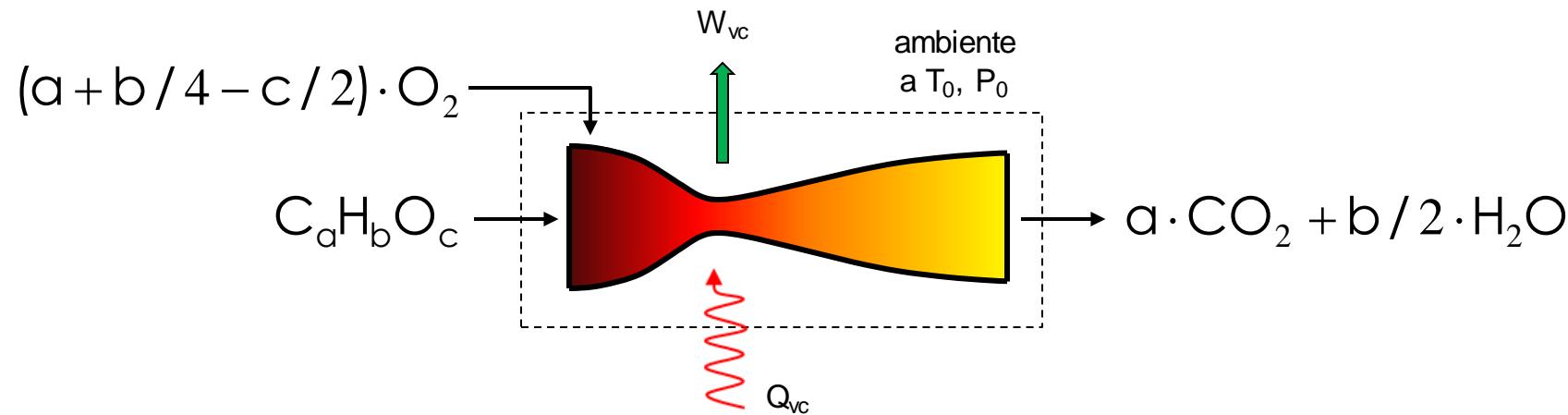
# Chemical exergy of substances not present in the environment

The chemical exergy of any substance can be determined considering its chemical transformation to the environment constituents ...



# Chemical exergy of substances not present in the environment

The chemical exergy of any substance can be determined considering its chemical transformation to the environment constituents ...



$$\frac{Q_{vc}}{n_F} - \frac{W_{vc}}{n_F} = [a \cdot h_{CO_2} + b/2 \cdot h_{H_2O}] - [h_F + (a + b/4 - c/2) \cdot h_{O_2}]$$

1<sup>ra</sup> Lei

$$\frac{Q_{vc}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F = 0$$

b. entropia

$$\frac{Q_{VC}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{VC}/n_F = 0 \quad b. \text{ entropia}$$

$$\frac{Q_{vc}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F = 0 \quad b. \text{ entropia}$$

$$Q_{vc} = -T_0 \cdot [s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F]$$

$$\frac{Q_{vc}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F = 0 \quad b. \text{ entropia}$$

$$Q_{vc} = -T_0 \cdot [s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F]$$

$$\rightarrow \frac{Q_{vc}}{n_F} - \frac{W_{vc}}{n_F} = [a \cdot h_{CO_2} + b/2 \cdot h_{H_2O}] - [h_F + (a + b/4 - c/2) \cdot h_{O_2}] \quad 1^{\text{ra}} \text{ Lei}$$

$$\frac{Q_{vc}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F = 0 \quad \text{b. entropia}$$

$$Q_{vc} = -T_0 \cdot [s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F]$$

$$\rightarrow \frac{Q_{vc}}{n_F} - \frac{W_{vc}}{n_F} = [a \cdot h_{CO_2} + b/2 \cdot h_{H_2O}] - [h_F + (a + b/4 - c/2) \cdot h_{O_2}] \quad \text{1ra Lei}$$

$$\frac{W_{vc}}{n_F} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right] - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2} - a \cdot s_{CO_2} - \frac{b}{2} \cdot s_{H_2O} \right] - T_0 \frac{\sigma_{vc}}{n_F}$$

$$\frac{Q_{vc}}{T_0} + s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F = 0 \quad \text{b. entropia}$$

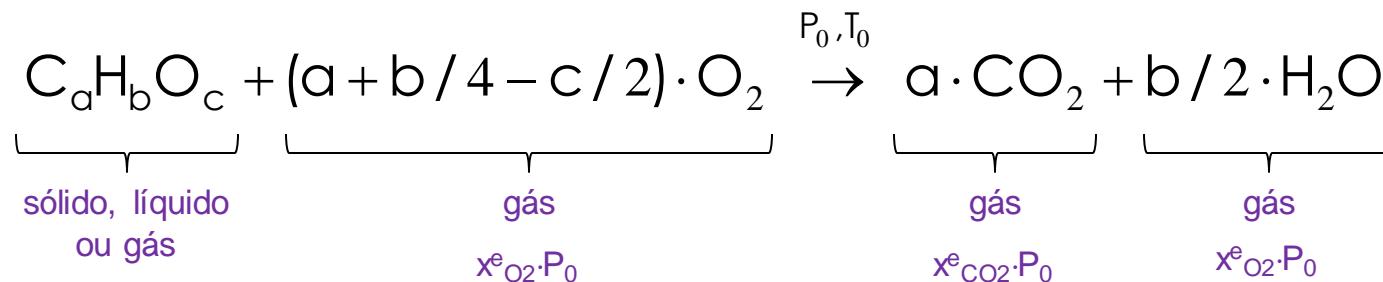
$$Q_{vc} = -T_0 \cdot [s_F + (a + b/4 - c/2) \cdot s_{O_2} - a \cdot s_{CO_2} - b/2 \cdot s_{H_2O} + \sigma_{vc}/n_F]$$

$$\frac{Q_{vc}}{n_F} - \frac{W_{vc}}{n_F} = [a \cdot h_{CO_2} + b/2 \cdot h_{H_2O}] - [h_F + (a + b/4 - c/2) \cdot h_{O_2}] \quad \text{1ra Lei}$$

$$\frac{W_{vc}}{n_F} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right] - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2} - a \cdot s_{CO_2} - \frac{b}{2} \cdot s_{H_2O} \right] - T_0 \frac{\sigma_{vc}}{n_F}$$

$$e_F^{ch} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right] - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2} - a \cdot s_{CO_2} - \frac{b}{2} \cdot s_{H_2O} \right]$$

Enthalpies and entropies are calculated at  $T_0$  and at the corresponding partial pressure of the environment component...



$$e_F^{ch} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2}(T_0) - a \cdot h_{CO_2}(T_0) - \frac{b}{2} \cdot h_{H_2O}(T_0) \right] + \dots$$

[ gás ideal,  $h = h(T)$  ]

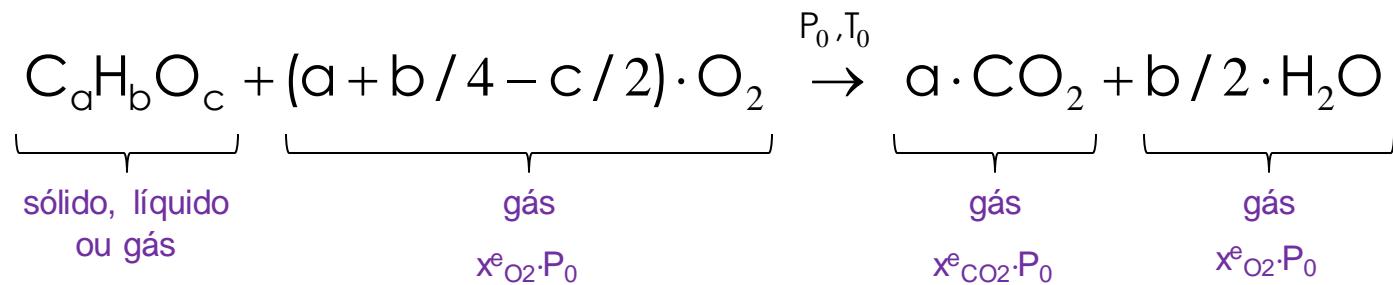
$$\dots - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2}(P_0, T_0) - a \cdot s_{CO_2}(x^e_{CO_2} \cdot P_0, T_0) - \frac{b}{2} \cdot s_{H_2O}(x^e_{H_2O} \cdot P_0, T_0) \right]$$

[ gás ideal,  $s = \dots$  ]

$$s_k(x_k^e \cdot P_0, T_0) = s_k(P_0, T_0) - R \cdot \ln(x_k^e)$$

$$ds = C_P \cdot \frac{dT}{T} - R \cdot \frac{dP}{P}$$

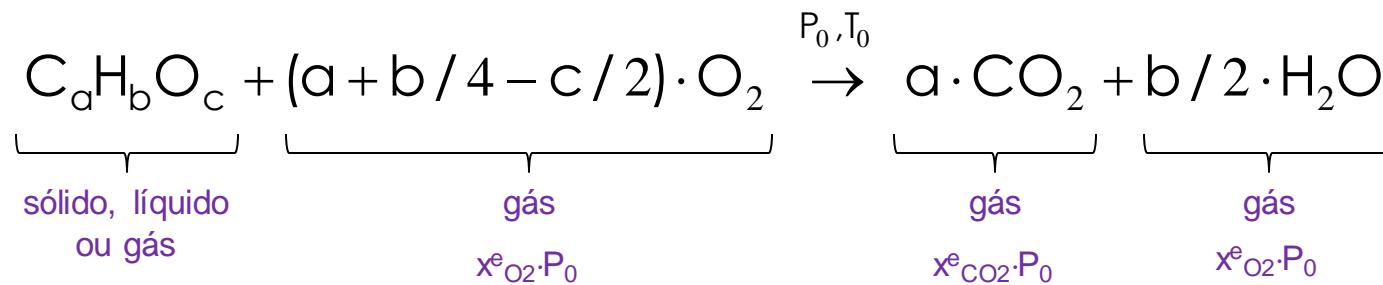
↑  
 ← gás ideal



$$e_F^{ch} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right]_{(P_0, T_0)} - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2} - a \cdot s_{CO_2} - \frac{b}{2} \cdot s_{H_2O} \right]_{(P_0, T_0)} + \dots$$

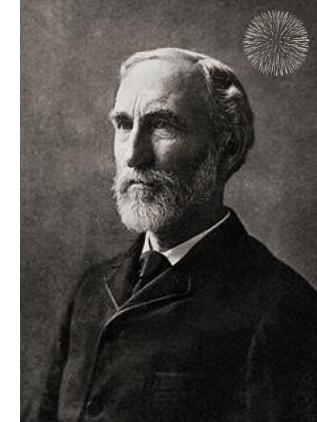
$$\dots + RT_0 \ln \left[ \frac{(x^e_{O_2})^{a+b/4-c/2}}{(x^e_{CO_2})^a \cdot (x^e_{H_2O})^{b/2}} \right]$$

Obs: se o componente for líquido ou sólido,  $x^e_{O_2} = 1$ .



$$e_F^{ch} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right]_{(P_0, T_0)} - T_0 \cdot \left[ S_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot S_{O_2} - a \cdot S_{CO_2} - \frac{b}{2} \cdot S_{H_2O} \right]_{(P_0, T_0)} + \dots$$

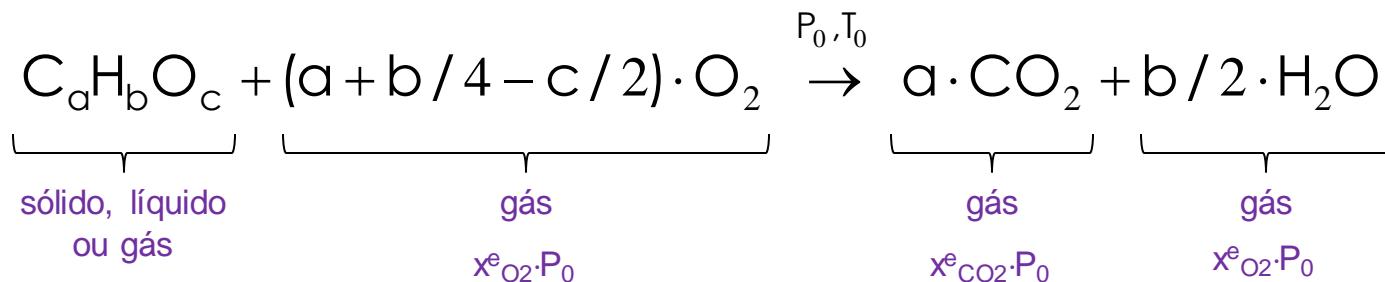
$$G \stackrel{\text{def}}{=} H - T \cdot S$$



J. Willard Gibbs

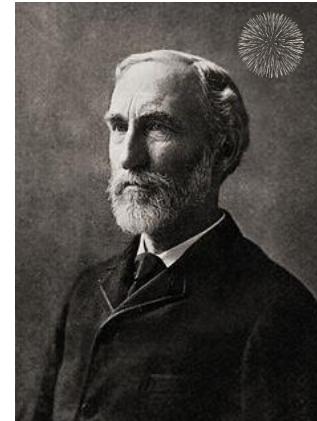
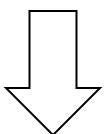
$$\dots + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

Obs: se o componente for líquido ou sólido,  $x_{O_2}^e = 1$ .



$$e_F^{ch} = \left[ h_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot h_{O_2} - a \cdot h_{CO_2} - \frac{b}{2} \cdot h_{H_2O} \right]_{(P_0, T_0)} - T_0 \cdot \left[ s_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot s_{O_2} - a \cdot s_{CO_2} - \frac{b}{2} \cdot s_{H_2O} \right]_{(P_0, T_0)} + \dots$$

$$G \stackrel{\text{def}}{=} H - T \cdot S$$



J. Willard Gibbs

$$\dots + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

Obs: se o componente for líquido ou sólido,  $x^e_{O_2} = 1$ .

$$e_F^{ch} = \left[ g_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot g_{O_2} - a \cdot g_{CO_2} - \frac{b}{2} \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

$$e_F^{ch} = \left[ g_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot g_{O_2} - a \cdot g_{CO_2} - \frac{b}{2} \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

Obs.1: the first term in the right side corresponds to the reaction's total Gibbs free energy variation... Therefore, the more spontaneous the greater the chemical exergy ...

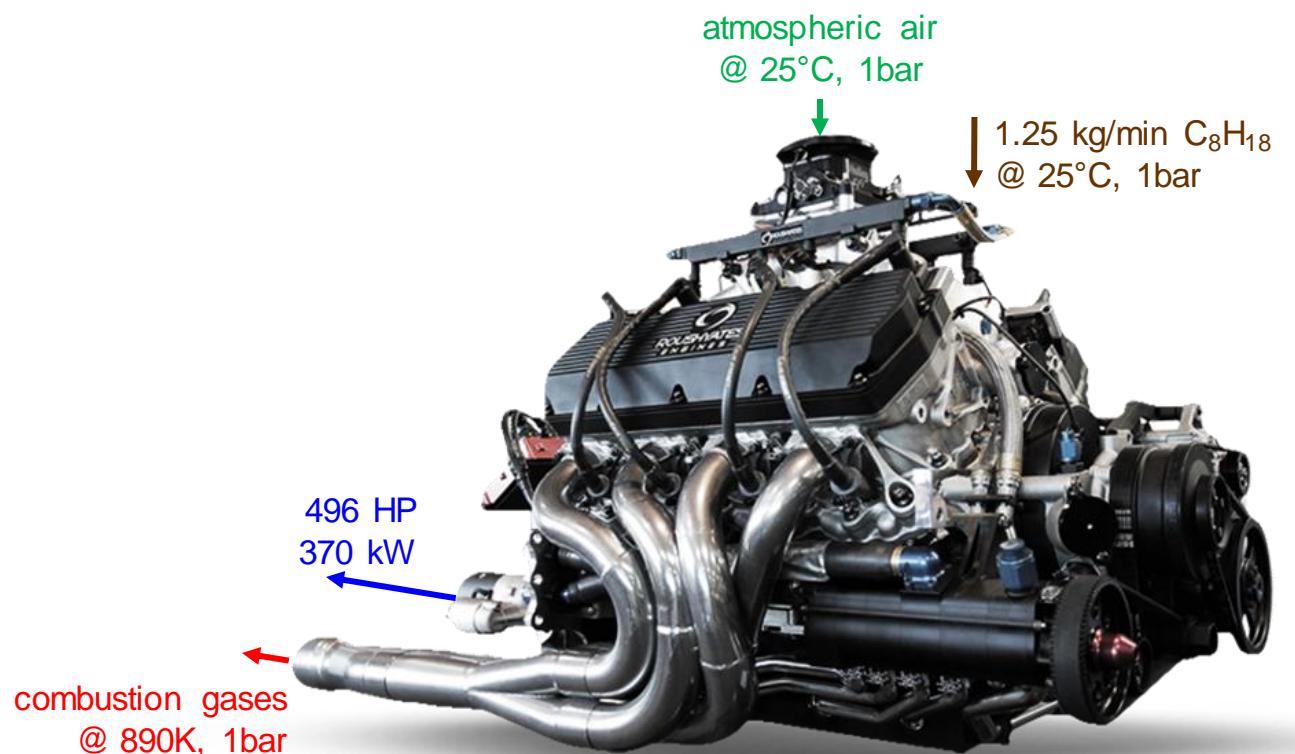
Obs.2: To bring all calculations to a common energy reference the Gibbs free energies can be calculated according to the following

$$g^\phi(T_0, P_0) = g_{formação}^\phi + [g(T_0, P_0) - g(T_{ref}, P_{ref})]$$

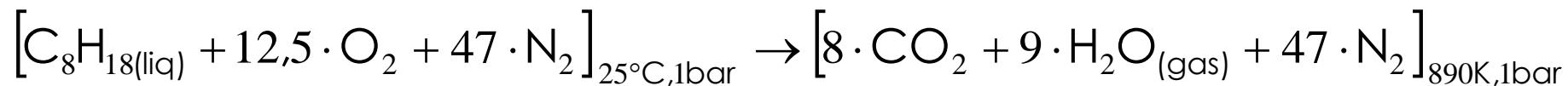


$$e_F^{ch} = -\Delta g + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

# Exergy analysis of an internal combustion engine



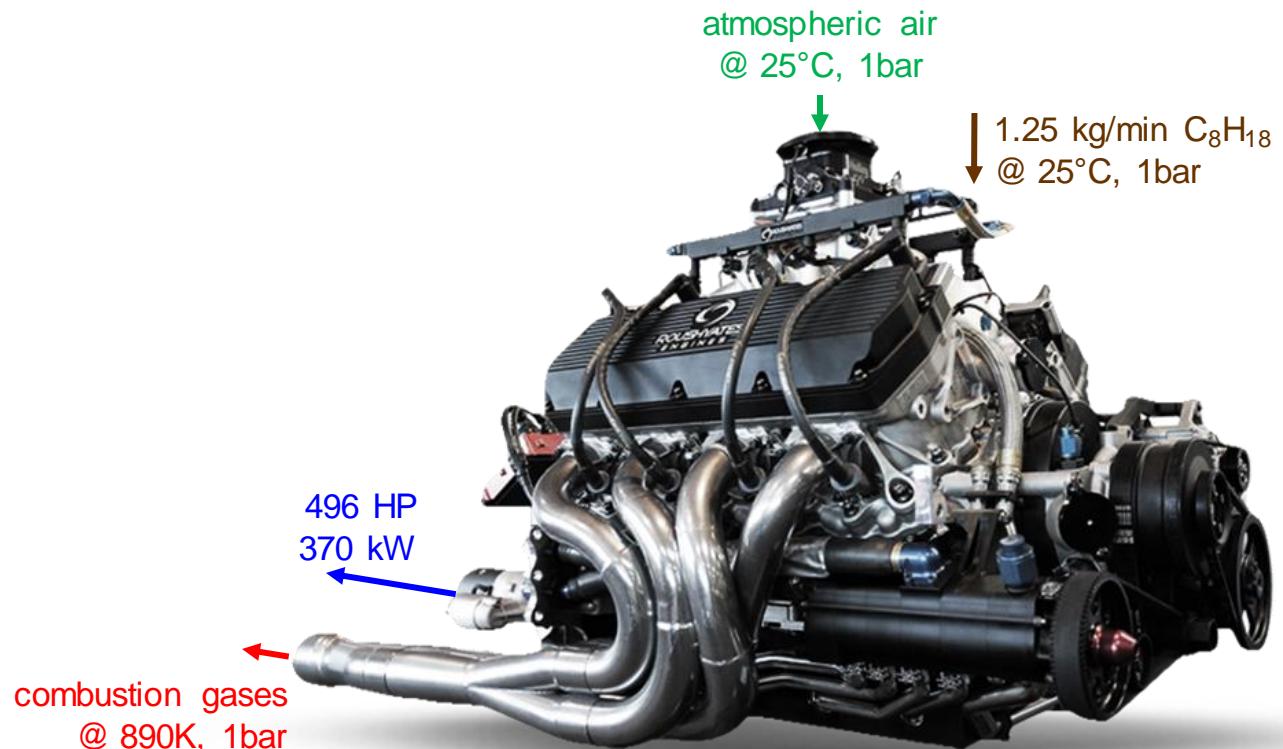
# Exergy analysis of an internal combustion engine



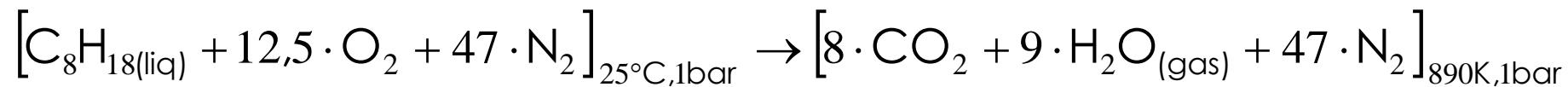
## Model do Environment

Temperature	$T_o = 298.15 \text{ K}$														
Pressure	$P_o = 1 \text{ atm}$														
Composition	(i) Atmospheric air saturated with $\text{H}_2\text{O}$ at $T_o$ and $P_o$ , having the following composition: <table border="1"><thead><tr><th>Air constituents</th><th>Mole fraction</th></tr></thead><tbody><tr><td><math>\text{N}_2</math></td><td>0.7567</td></tr><tr><td><math>\text{O}_2</math></td><td>0.2035</td></tr><tr><td><math>\text{H}_2\text{O}</math></td><td>0.0303</td></tr><tr><td>Ar</td><td>0.0091</td></tr><tr><td><math>\text{CO}_2</math></td><td>0.0003</td></tr><tr><td><math>\text{H}_2</math></td><td>0.0001</td></tr></tbody></table>	Air constituents	Mole fraction	$\text{N}_2$	0.7567	$\text{O}_2$	0.2035	$\text{H}_2\text{O}$	0.0303	Ar	0.0091	$\text{CO}_2$	0.0003	$\text{H}_2$	0.0001
Air constituents	Mole fraction														
$\text{N}_2$	0.7567														
$\text{O}_2$	0.2035														
$\text{H}_2\text{O}$	0.0303														
Ar	0.0091														
$\text{CO}_2$	0.0003														
$\text{H}_2$	0.0001														
	(ii) The following condensed phases at $T_o$ and $P_o$ : Water ( $\text{H}_2\text{O}$ ) Limestone ( $\text{CaCO}_3$ ) Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )														

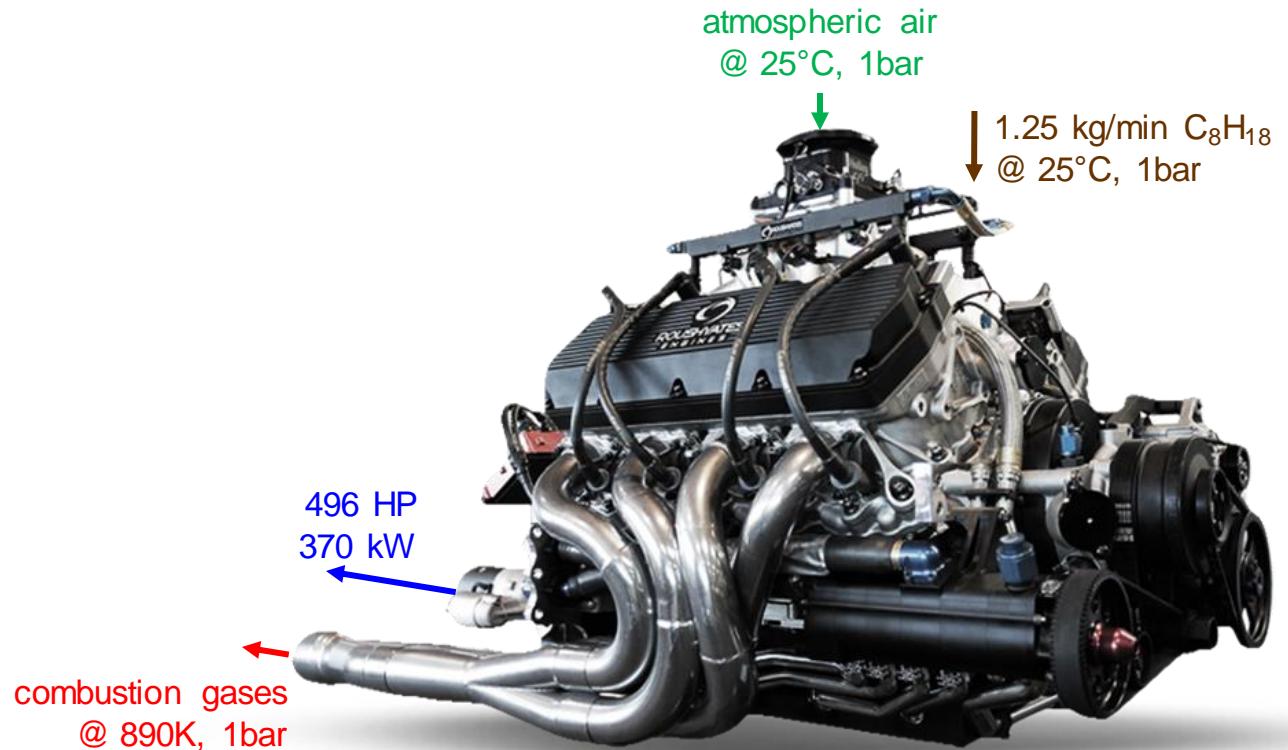
Source: Adapted from Gaggioli and Petit (1977).



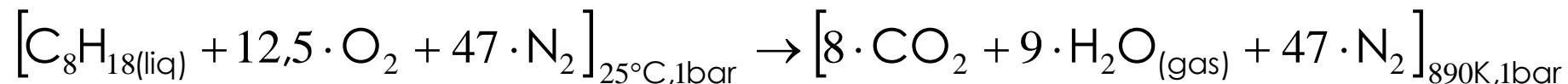
# Exergy analysis of an internal combustion engine



$$1^{\text{ra}} \text{ Lei} \rightarrow Q_{vc} - W_{vc} = n_F \cdot \left( \sum_{\text{prod}} h_k - \sum_{\text{reag}} h_k \right)$$



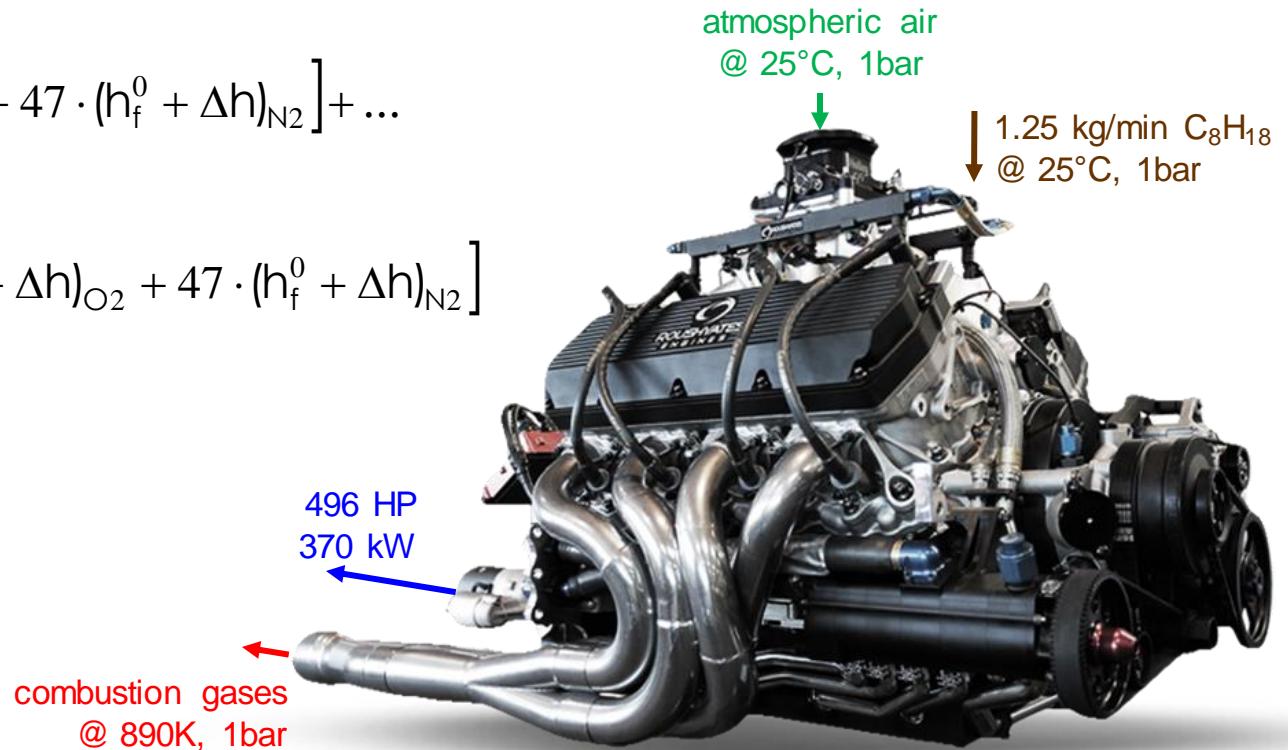
# Exergy analysis of an internal combustion engine



1<sup>ra</sup> Lei →  $Q_{vc} - W_{vc} = n_F \cdot \left( \sum_{prod} h_k - \sum_{reag} h_k \right)$

$$\frac{Q_{vc} - W_{vc}}{n_F} = [8 \cdot (h_f^0 + \Delta h)_{CO_2} + 9 \cdot (h_f^0 + \Delta h)_{H_2O(g)} + 47 \cdot (h_f^0 + \Delta h)_{N_2}] + \dots$$

$$\dots - [1 \cdot (h_f^0 + \Delta h)_{C_8H_{18(liq)}} + 12,5 \cdot (h_f^0 + \Delta h)_{O_2} + 47 \cdot (h_f^0 + \Delta h)_{N_2}]$$



# Exergy analysis of an internal combustion engine

$$\frac{Q_{vc} - W_{vc}}{n_F} = \left[ 8 \cdot (h_f^0 + \Delta h)_{CO_2} + 9 \cdot (h_f^0 + \Delta h)_{H_2O(g)} + 47 \cdot (h_f^0 + \Delta h)_{N_2} \right]_{890K, 1bar} + \dots$$
$$\dots - \left[ 1 \cdot (h_f^0 + \Delta h)_{C8H18(liq)} + 12,5 \cdot (h_f^0 + \Delta h)_{O_2} + 47 \cdot (h_f^0 + \Delta h)_{N_2} \right]_{25^\circ C, 1bar}$$

~~$=0$~~        ~~$=0$~~        ~~$=0$~~        ~~$=0$~~        ~~$=0$~~        ~~$=0$~~

Entalpias de formação

$$h_{f,C8H18(liq)}^0 = -249.910 \text{ kJ/mol}$$

$$h_{f,CO_2(g)}^0 = -393.520 \text{ kJ/mol}$$

$$h_{f,H_2O(g)}^0 = -241.820 \text{ kJ/mol}$$

Entalpias sensíveis

$$P_{CO_2} = 8 / (8 + 9 + 47) \cdot 1 = 0,125 \text{ bar} \rightarrow h_{CO_2}(890K) = 49.811 \text{ kJ/mol}$$

$$\rightarrow h_{CO_2}(298K) = 22.293 \text{ kJ/mol}$$

$$P_{N_2} = 47 / (8 + 9 + 47) \cdot 1 = 0,734 \text{ bar} \rightarrow h_{N_2}(890K) = 26.573 \text{ kJ/mol}$$

$$\rightarrow h_{N_2}(298K) = 8.661 \text{ kJ/mol}$$

$$P_{H_2O} = 9 / (8 + 9 + 47) \cdot 1 = 0,141 \text{ bar} \rightarrow h_{H_2O}(890K) = 65.472 \text{ kJ/mol}$$

$$\rightarrow h_{H_2O}(298K) = 45.871 \text{ kJ/mol}$$

$$\rightarrow h_{H_2O}(298K) = 1.877 \text{ kJ/mol}$$

# Exergy analysis of an internal combustion engine

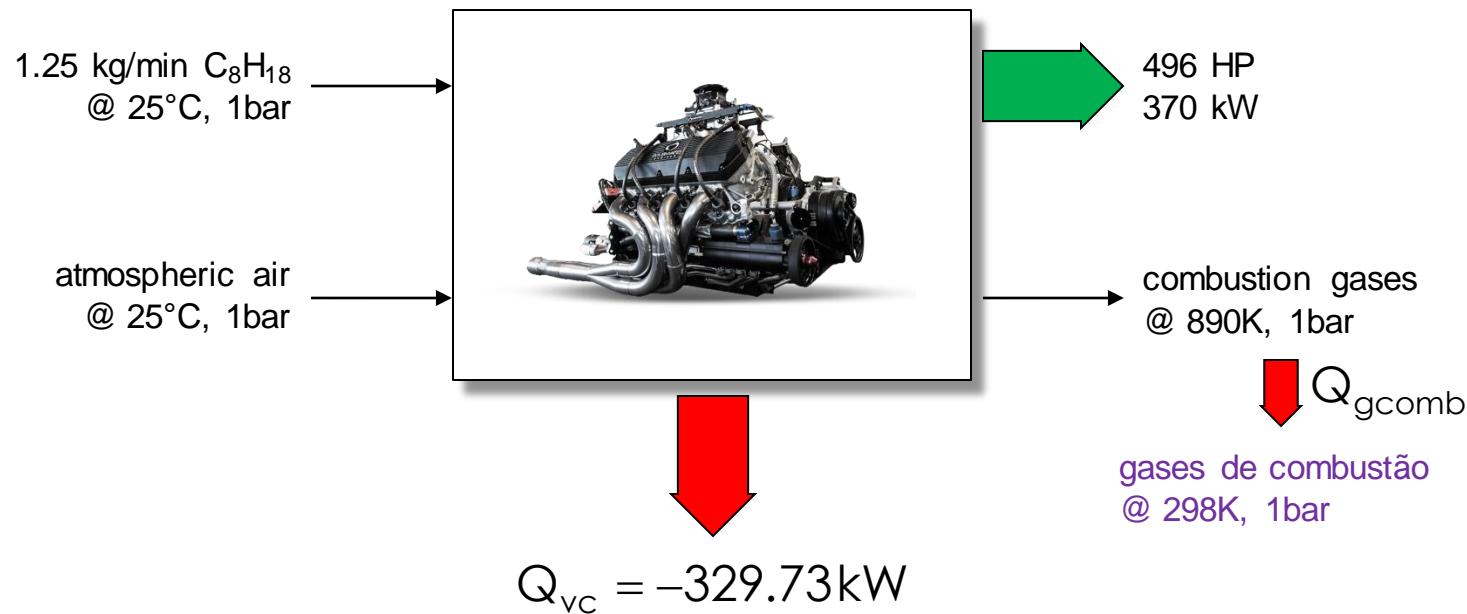
$$\frac{Q_{vc} - W_{vc}}{n_F} = \left[ 8 \cdot (h_f^0 + \Delta h)_{CO_2} + 9 \cdot (h_f^0 + \Delta h)_{H_2O(g)} + 47 \cdot (h_f^0 + \Delta h)_{N_2} \right]_{890K, 1bar} + \dots$$
$$\dots - \left[ 1 \cdot (h_f^0 + \Delta h)_{C8H18(liq)} + 12.5 \cdot (h_f^0 + \Delta h)_{O_2} + 47 \cdot (h_f^0 + \Delta h)_{N_2} \right]_{25^\circ C, 1bar}$$

$\cancel{=0}$        $\cancel{=0}$        $\cancel{=0}$        $\cancel{=0}$        $\cancel{=0}$        $\cancel{=0}$

$$\frac{\frac{Q_{vc} - 370}{1.25}}{\frac{1}{60} \cdot \frac{1}{0.11422}} = [8 \cdot (-393.52 + 49.81 - 22.29) + 9 \cdot (-241.82 + 65.472 - 45.871) + 47 \cdot (0 + 26.57 - 8.66)] + 249.91$$

$$Q_{vc} = -329.73 \text{ kW}$$

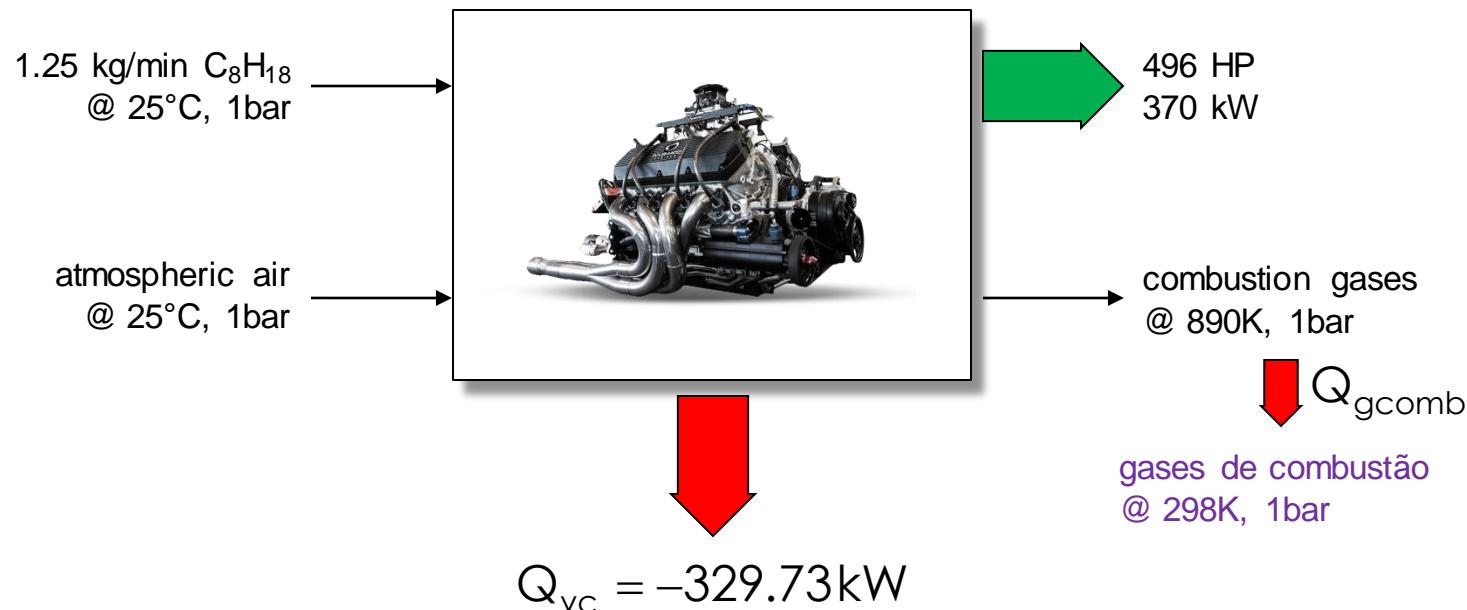
# Exergy analysis of an internal combustion engine



$$\eta_{1^\circ\text{Lei}} = \frac{\text{shaft mechanical power}}{\text{supplied heat}} \leq \eta_{\max}$$

$$\eta_{1^\circ\text{Lei}} = \frac{W_{\text{eixo}}}{W_{\text{eixo}} + Q_{\text{vc}} + Q_{\text{gcomb}}} \leq \eta_{\max}$$

# Exergy analysis of an internal combustion engine



$$h_{CO_2}(890K) = 49.811\text{kJ/mol}$$

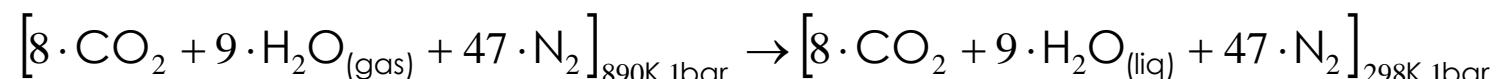
$$h_{CO_2}(298K) = 22.293\text{kJ/mol}$$

$$h_{N_2}(890K) = 26.573\text{kJ/mol}$$

$$h_{N_2}(298K) = 8.661\text{kJ/mol}$$

$$h_{H_2O}(890K) = 67.439\text{kJ/mol}$$

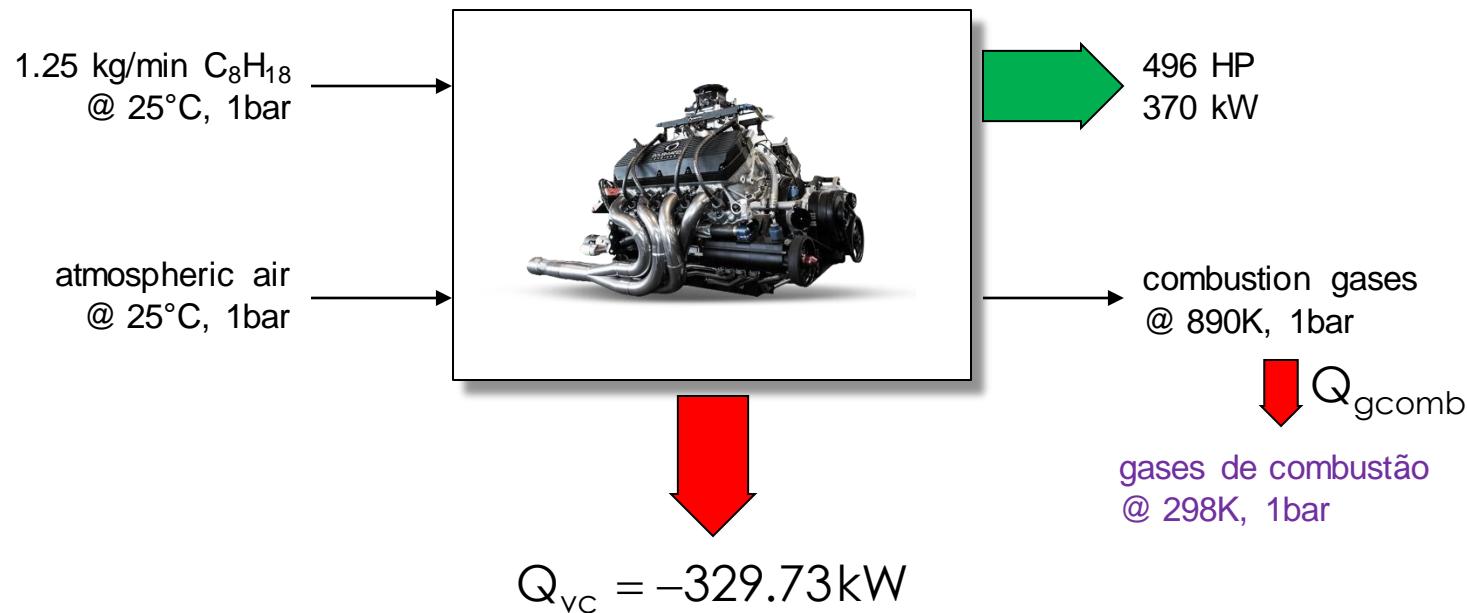
$$h_{H_2O}(298K) = 45.871\text{kJ/mol}$$



$$\frac{Q_{gcomb}}{1.25/60/0.11422} = [8 \cdot h_{CO_2} + 9 \cdot h_{H_2O} + 47 \cdot h_{N_2}]_{298K, 1bar} - [8 \cdot h_{CO_2} + 9 \cdot h_{H_2O} + 47 \cdot h_{N_2}]_{890K, 1bar}$$

$$\frac{Q_{gcomb}}{1.25/60/0.11422} = 8 \cdot (22.293 - 49.811) + 9 \cdot (1.877 - 65.472) + 47 \cdot (8.661 - 26.573) \Rightarrow -298.088\text{kW}$$

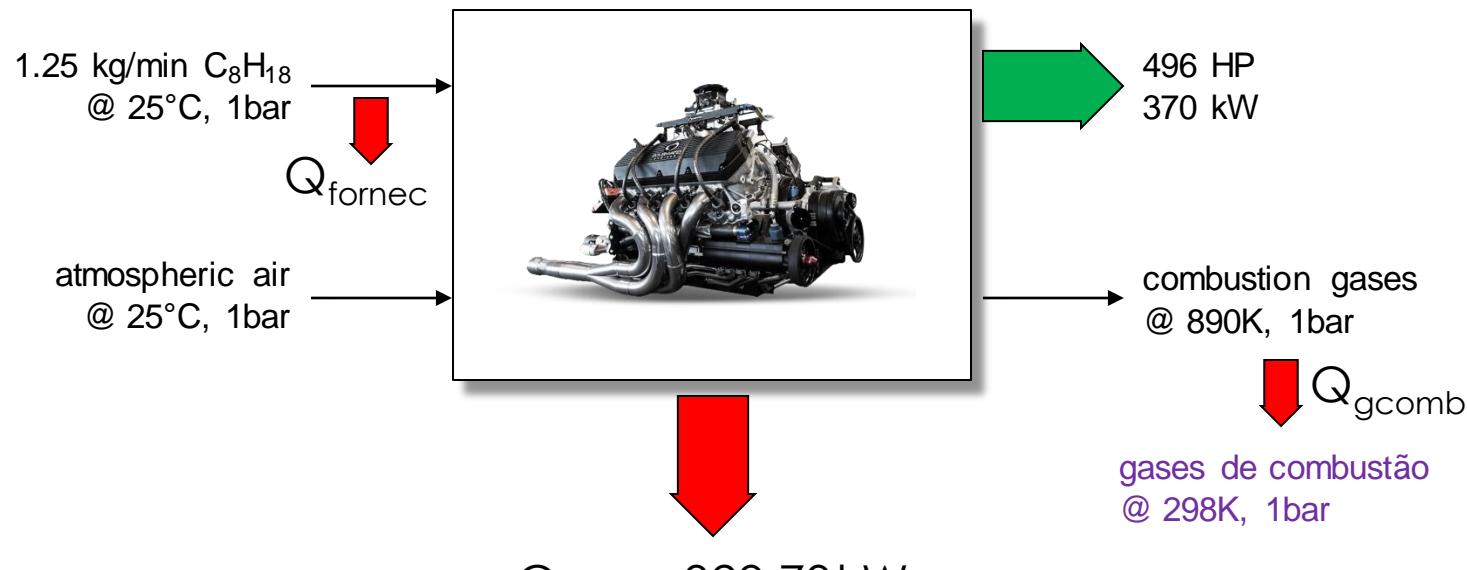
# Exergy analysis of an internal combustion engine



$$Q_{\text{fornec}} = W_{\text{eixo}} + Q_{\text{vc}} + Q_{\text{gcomb}}$$

$$Q_{\text{fornec}} = 370 + 329.726 + 298.088 = 997.814 \text{ kW}$$

# Exergy analysis of an internal combustion engine



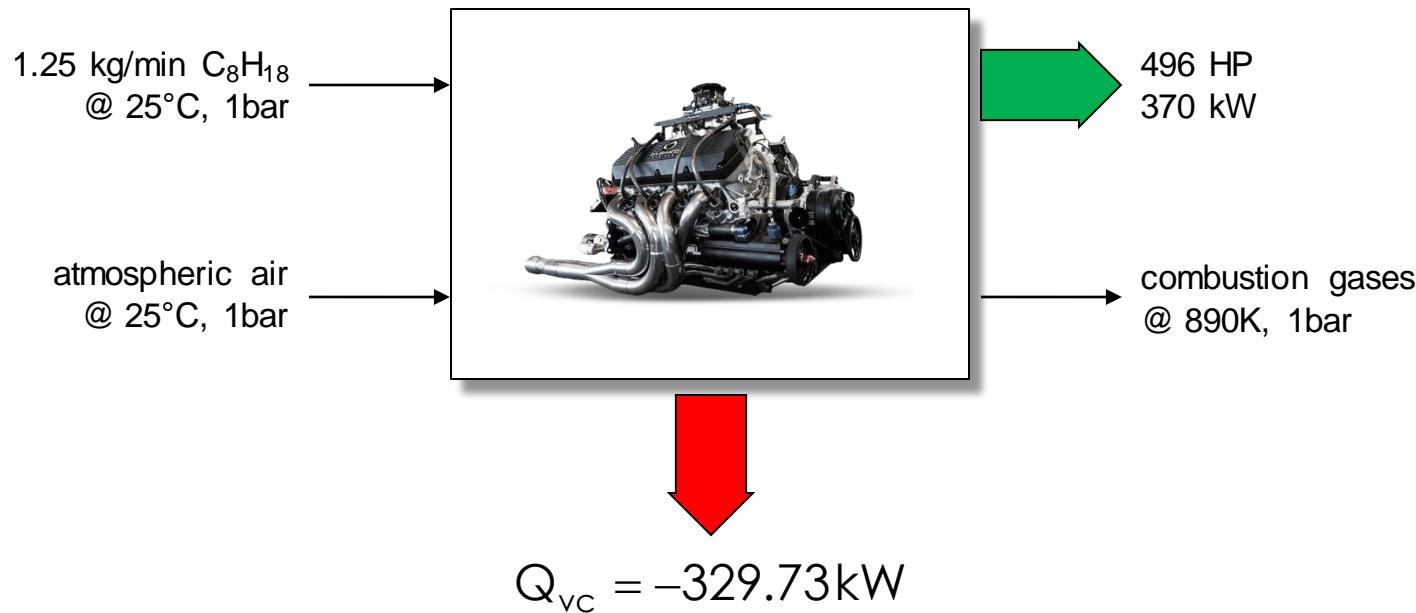
Heating Values		
	Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Substance		
Butane	49,500	45,720
Pentane	49,010	45,350
Octane	48,260	44,790
Octane	47,900	44,430
Benzene	42,270	40,580

$$Q_{\text{fornec}} = W_{\text{eixo}} + Q_{\text{vc}} + Q_{\text{gcomb}}$$

$$Q_{\text{fornec}} = 370 + 329.726 + 298.088 = 997.814\text{kW}$$

$$Q_{\text{fornec}} = \frac{1.25}{60} 48260 = 1005.417\text{kW}$$

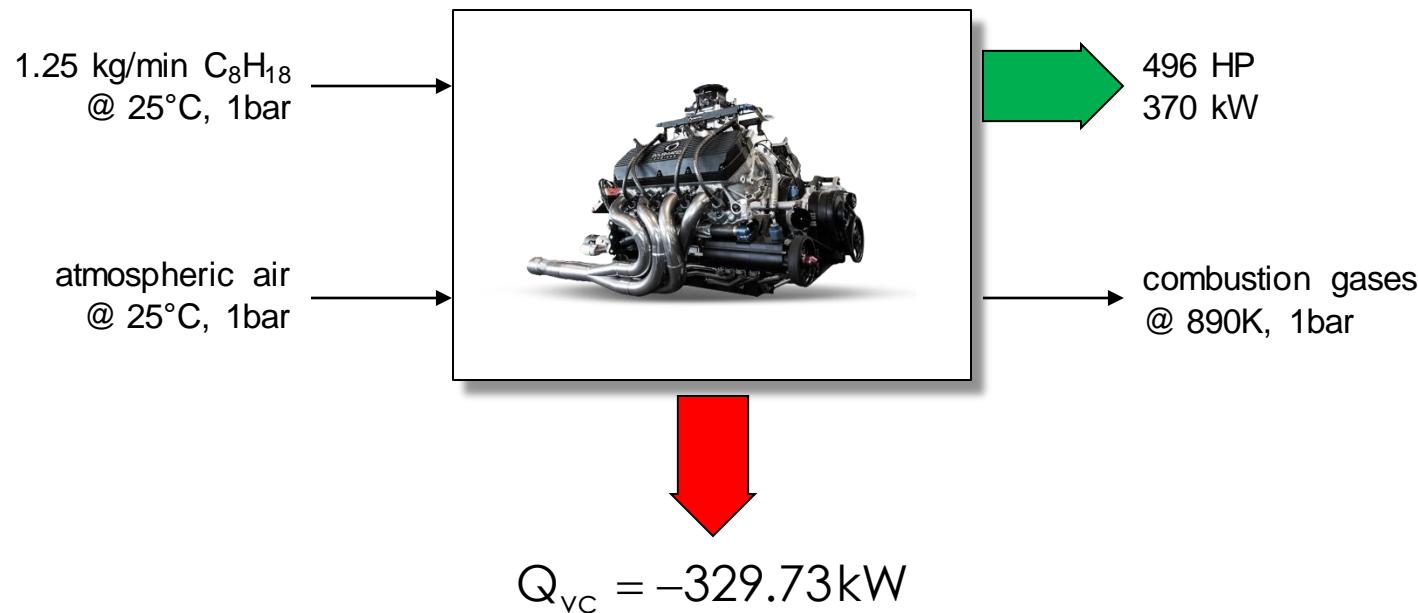
# Exergy analysis of an internal combustion engine



$$\eta_{1^{\circ}\text{Lei}} = \frac{\text{pot.mecânica líquida}}{\text{calor fornecido}} \leq \eta_{\max}$$

$$\eta_{1^{\circ}\text{Lei}} = \frac{370}{370 + 329.726 + 298.814} = 37.1\% \leq \eta_{\max} \quad ?!?$$

# Exergy analysis of an internal combustion engine



$$\eta_{2^\circ\text{Lei}} = \frac{\text{available exergy}}{\text{supplied exergy}}$$

# Exergy analysis of an internal combustion engine

Supplied exergy corresponds to the maximum mechanical power that can be obtained when fuel is being chemically transformed to the environment components..

Compounds present in the environment

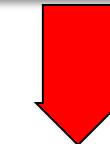
atmospheric air  
@ 25°C, 1bar

1.25 kg/min C<sub>8</sub>H<sub>18</sub>  
@ 25°C, 1bar



496 HP  
370 kW

combustion gases  
@ 890K, 1bar



$$Q_{vc} = -329.73 \text{ kW}$$

$$\eta_{2^\circ\text{Lei}} = \frac{\text{available exergy}}{\text{supplied exergy}}$$

$$\eta_{2^\circ\text{Lei}} = \frac{\text{shaft mechanical power}}{\text{fuel exergy content}}$$

# Exergy analysis of an internal combustion engine

$$e_F^{ch} = \left[ g_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot g_{O_2} - a \cdot g_{CO_2} - \frac{b}{2} \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

C<sub>8</sub>H<sub>18</sub>  a=8, b=18, c=0

$$e_F^{ch} = \left[ g_F + 12.5 \cdot g_{O_2} - 8 \cdot g_{CO_2} - 9 \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{12.5}}{(x_{CO_2}^e)^8 \cdot (x_{H_2O}^e)^9} \right]$$

$$x_{N_2}^e = 0.7567 \text{ molar}$$

$$x_{O_2}^e = 0.2035 \text{ molar}$$

$$x_{CO_2}^e = 0.0003 \text{ molar}$$

$$x_{H_2O}^e = 0.0312 \text{ molar}$$

 Mto variável...

$$g_F^{\phi=0} = 6.610 \text{ kJ/mol}$$

$$g_{O_2}^{\phi=0} = 0 \text{ kJ/mol}$$

$$g_{CO_2}^{\phi=0} = -394.38 \text{ kJ/mol}$$

$$g_{H_2O}^{\phi=0} = -228.59 \text{ kJ/mol}$$

# Exergy analysis of an internal combustion engine

$$e_F^{ch} = \left[ g_F + \left( a + \frac{b}{4} - \frac{c}{2} \right) \cdot g_{O_2} - a \cdot g_{CO_2} - \frac{b}{2} \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{a+b/4-c/2}}{(x_{CO_2}^e)^a \cdot (x_{H_2O}^e)^{b/2}} \right]$$

C<sub>8</sub>H<sub>18</sub>  a=8, b=18, c=0

$$e_F^{ch} = \left[ g_F + 12.5 \cdot g_{O_2} - 8 \cdot g_{CO_2} - 9 \cdot g_{H_2O} \right]_{(P_0, T_0)} + RT_0 \ln \left[ \frac{(x_{O_2}^e)^{12.5}}{(x_{CO_2}^e)^8 \cdot (x_{H_2O}^e)^9} \right]$$



$$e_F^{ch} = [6.61 + 12.5 \cdot 0 - 8 \cdot (-394.38) - 9 \cdot (-228.59)] + 8.314 \cdot 298 \cdot \ln \left[ \frac{0.2035^{12.5}}{0.0003^8 \cdot 0.0312^9} \right]$$

$$e_F^{ch} = 5407.843 \text{ kJ/mol}$$

# Exergy analysis of an internal combustion engine

$$e_F^{ch} = 5407.843 \text{ kJ/mol}$$

$$W_F^{ch} = 5407.843 \frac{\text{kJ}}{\text{mol}} \times 1.25 \frac{\text{kg}}{60\text{s}} \times \frac{1}{0.11422 \text{ kg/mol}}$$

$$W_F^{ch} = 986.372 \text{ kW}$$

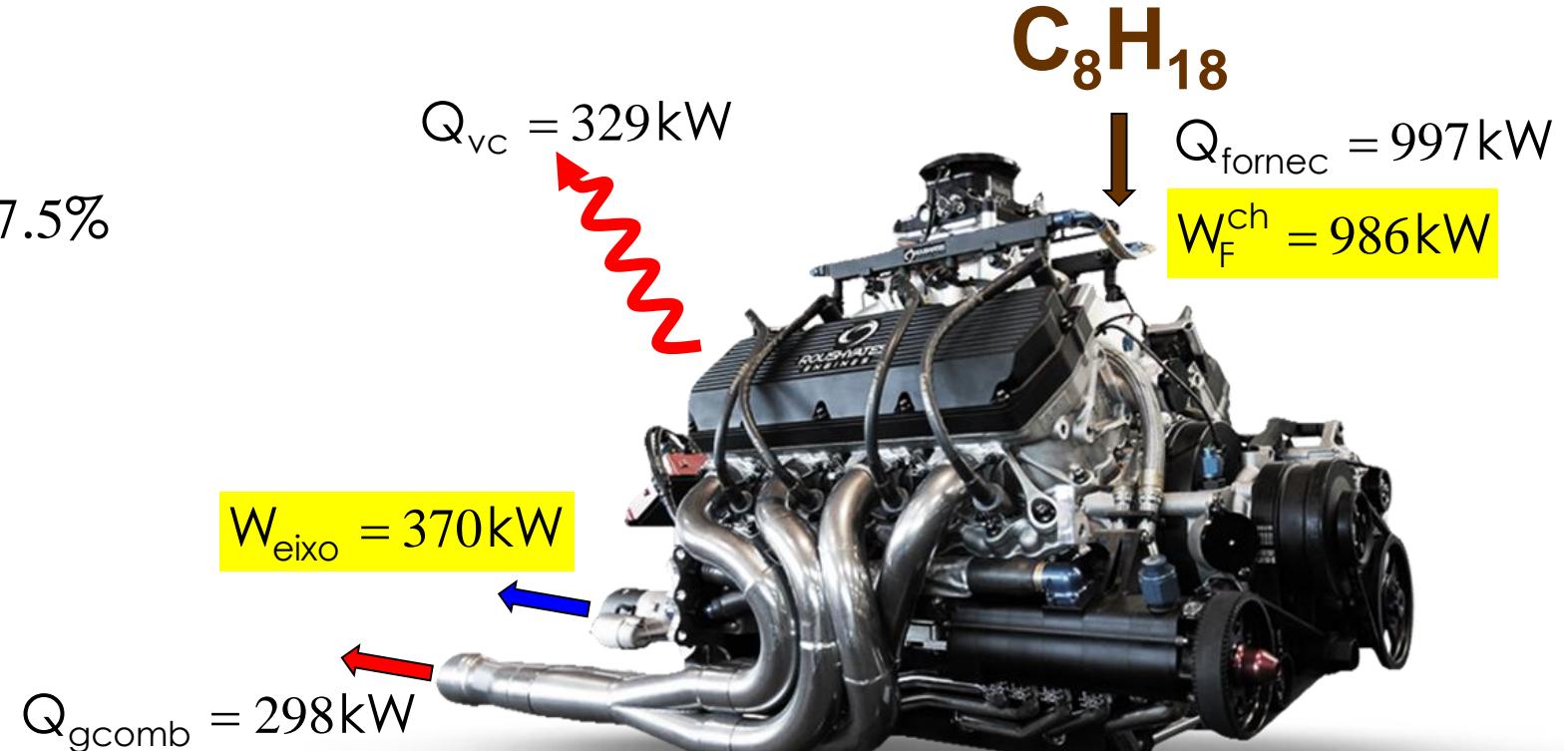
$$\eta_{2^{\circ}\text{Lei}} = \frac{\text{shaft mechanical power}}{\text{fuel exergy content}}$$

$$\eta_{2^{\circ}\text{Lei}} = \frac{370}{986.372} = 37.5\%$$

# Exergy analysis of an internal combustion engine

$$\eta_{1^\circ\text{Lei}} = \frac{W_{\text{eixo}}}{Q_{\text{fornec}}} = 37.1\%$$

$$\eta_{2^\circ\text{Lei}} = \frac{W_{\text{eixo}}}{W_F^{\text{ch}}} = 37.5\%$$





How does batteries compare with liquid fuels in terms of energy storage ?

"volumetric" density → smaller

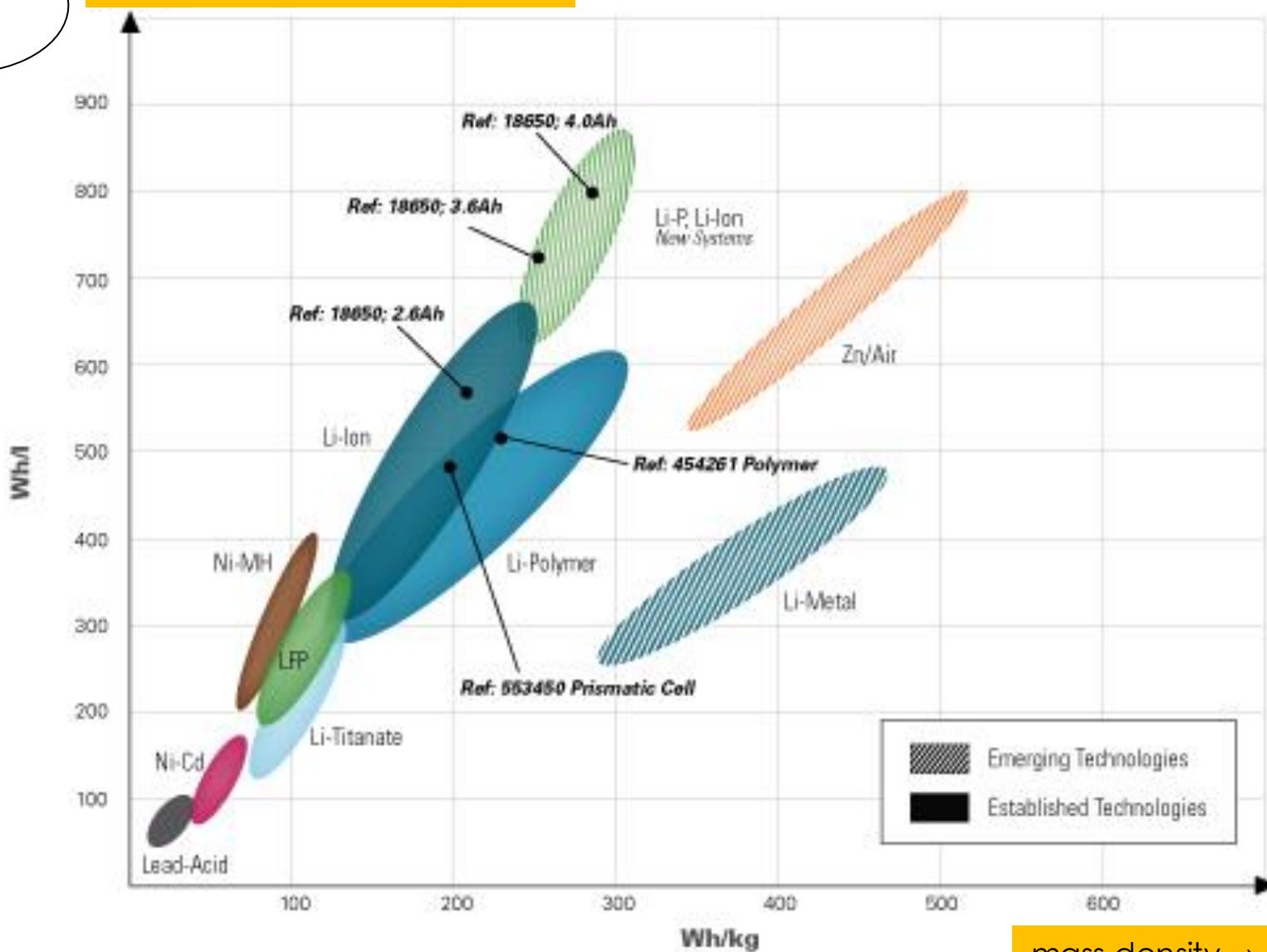


mass density → lighter

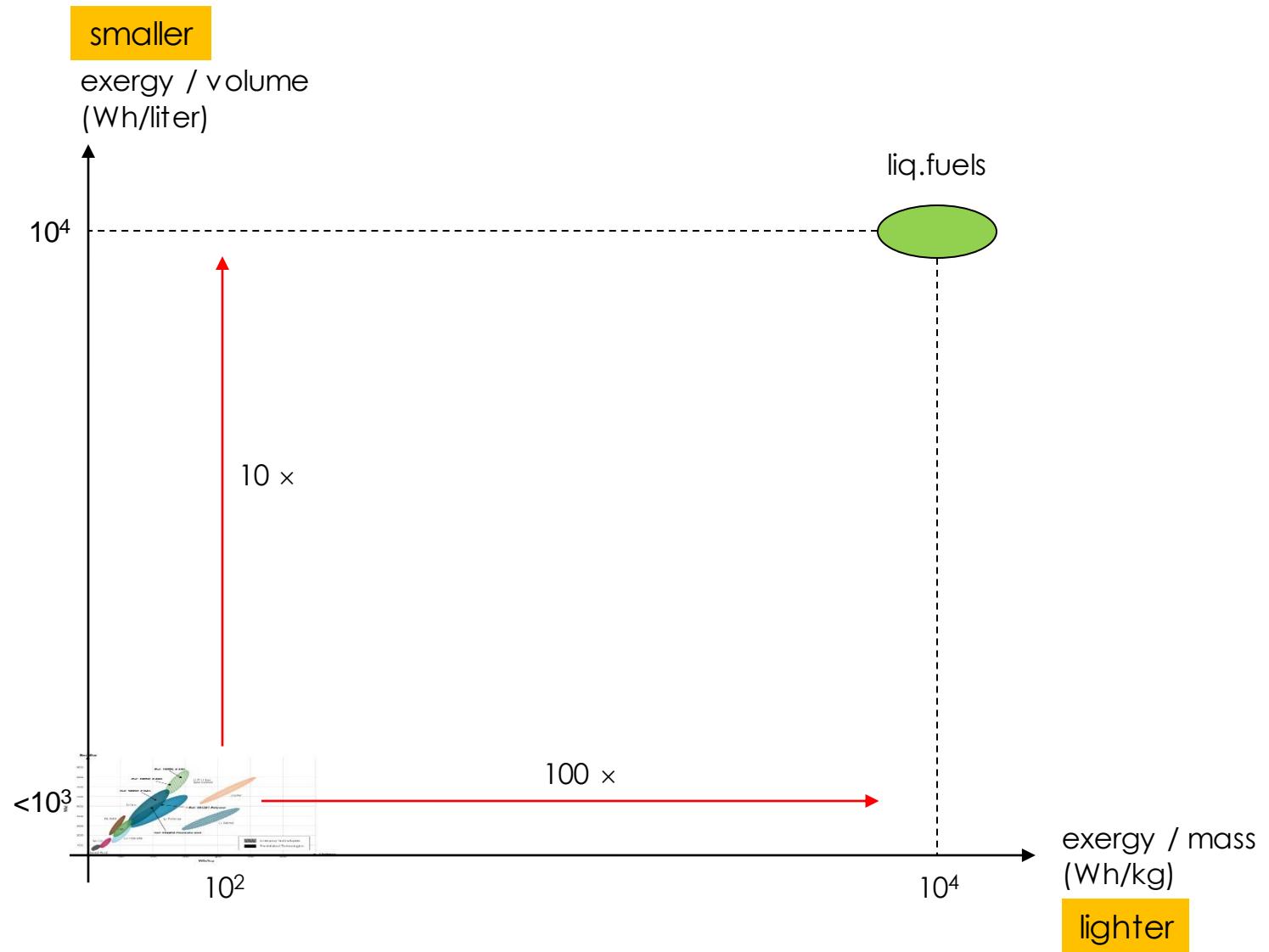
How does batteries compare with liquid fuels in terms of energy storage ?



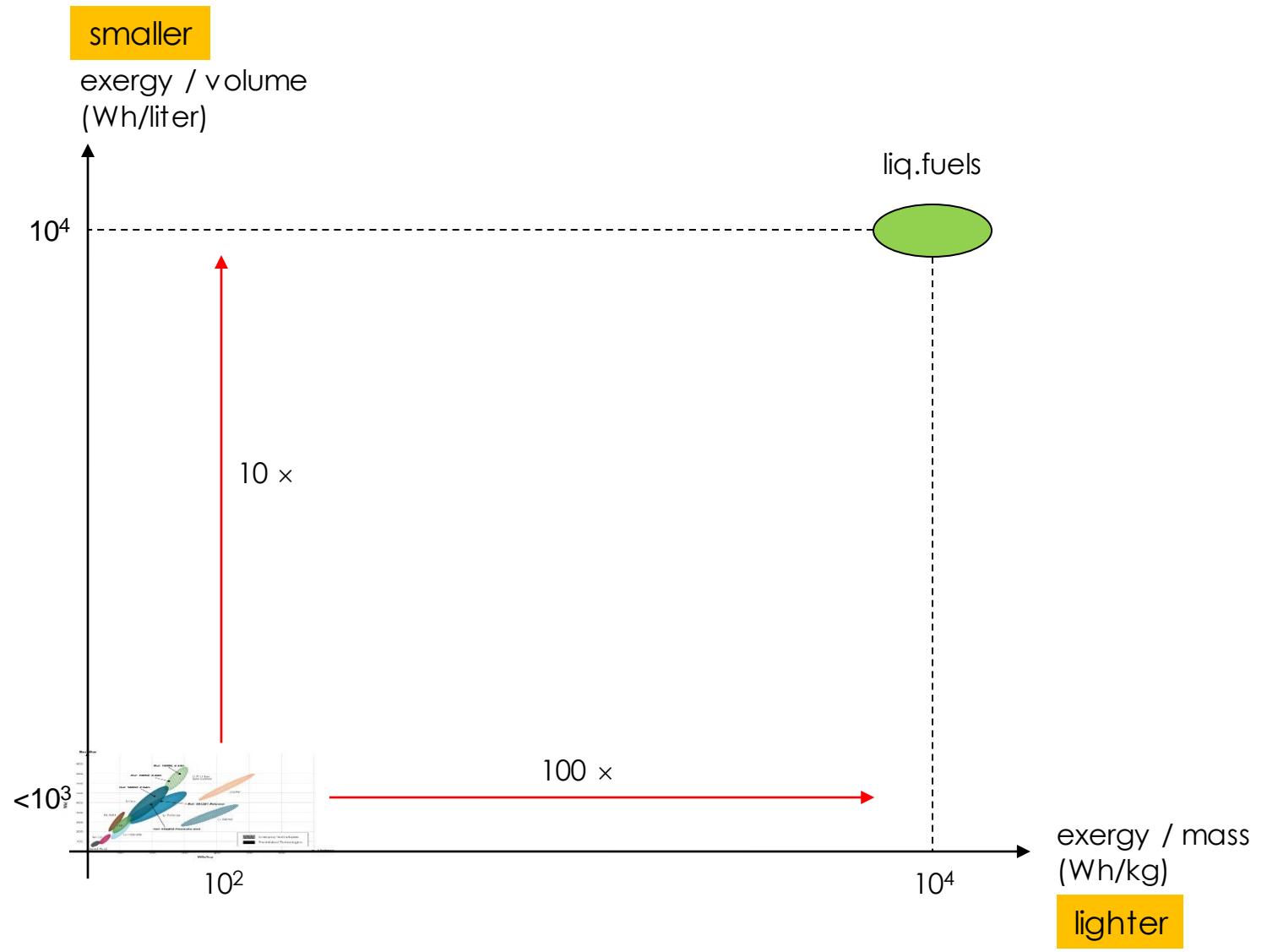
"volumetric" density → smaller



How does batteries compare with liquid fuels in terms of energy storage ?

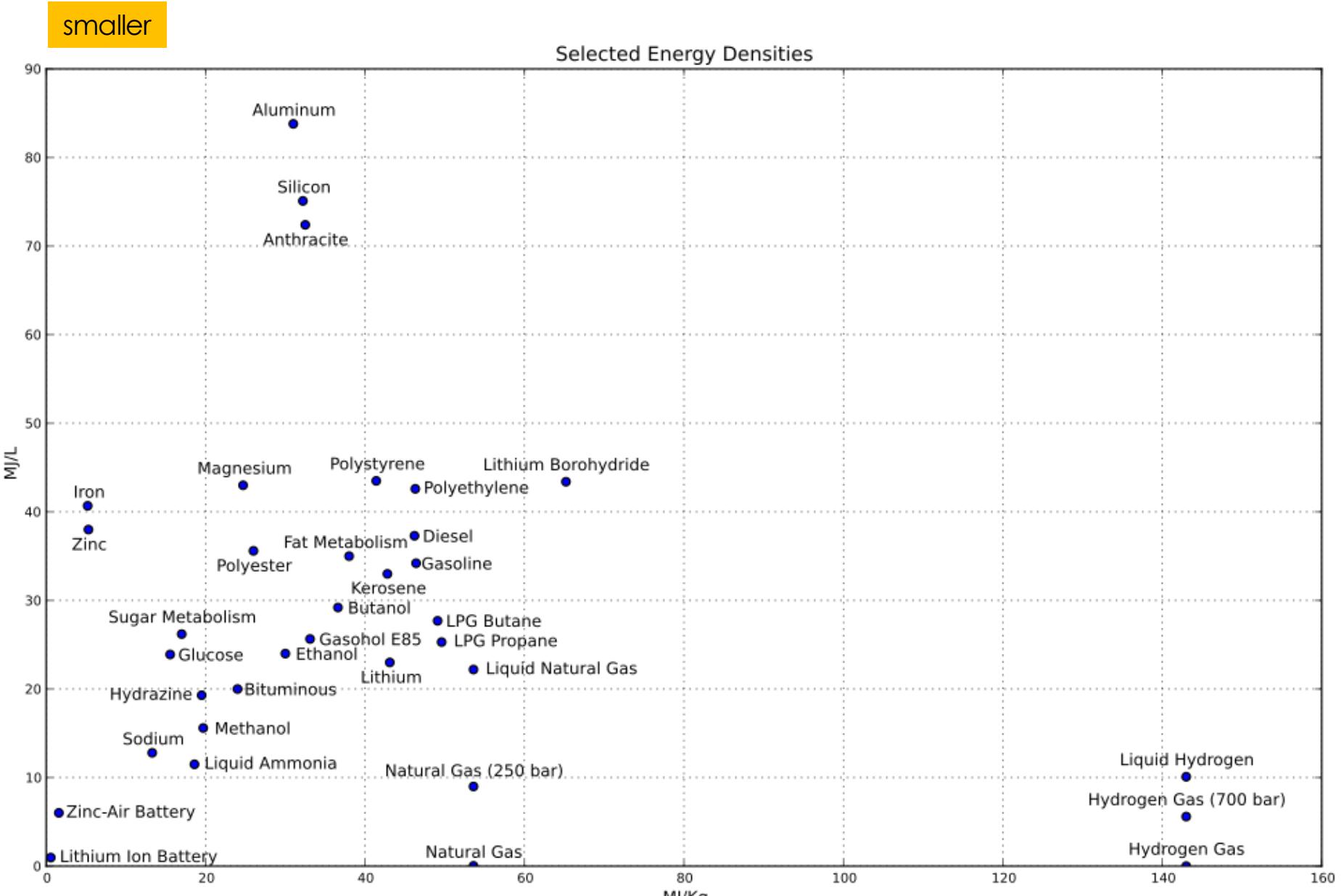


Hybrid cars...





Propellant fuel: PBAN-APCP



Paulo Seleg him - YouTube

https://www.youtube.com/channel/UCn46\_J-tZOormY24CqhDQ

Pesquisar

YouTube BR

Search

Upload

Home

My Channel

Trending

Subscriptions 39

History

Watch Later

LIBRARY

Curso de Energias Re...

Heroes Of The Enlight...

Lectures

Show more

SUBSCRIPTIONS

Os Pingos nos Is... 4

TV USP Piracicaba 1

Yuval Noah Harari 1

Technologyguru 5

World Science Fe... 1

stanfordonline 1

DIE ANTWOORD ... 5

Idson Ricart

MIT Club of Nort... 1

StarTalk Radio 2

Applied Science 1

MIT OpenCourse... 2

MBAbullshitDotCom

EducateKnowledge

2,147 subscribers 203,887 views Video Manager

Paulo Seleg him View as: Yourself

Blogger G+

Subscribe 2,147

Home Videos Playlists Channels Discussion About

For returning subscribers For new visitors

What to watch next

Ao Vivo: Energia Livre de Gibbs by Paulo Seleg him 7 views 2 hours ago

Ao Vivo: Conservação de Energia em reações Químicas by Paulo Seleg him 57 views 4 days ago

Ao Vivo: MISTURA DE GASES: equilíbrio de fases e a lei de Raoult by Paulo Seleg him 53 views 1 week ago

Ao Vivo: Turbinas para a Conversão de Energia de Fluxo by Paulo Seleg him 87 views 1 week ago

Channel tips

- 6 tips to build community
- Get local updates
- Filming on your phone
- Get discovered
- Analytics boot camp
- What cards can do for you

View all »

None

+ Add channels

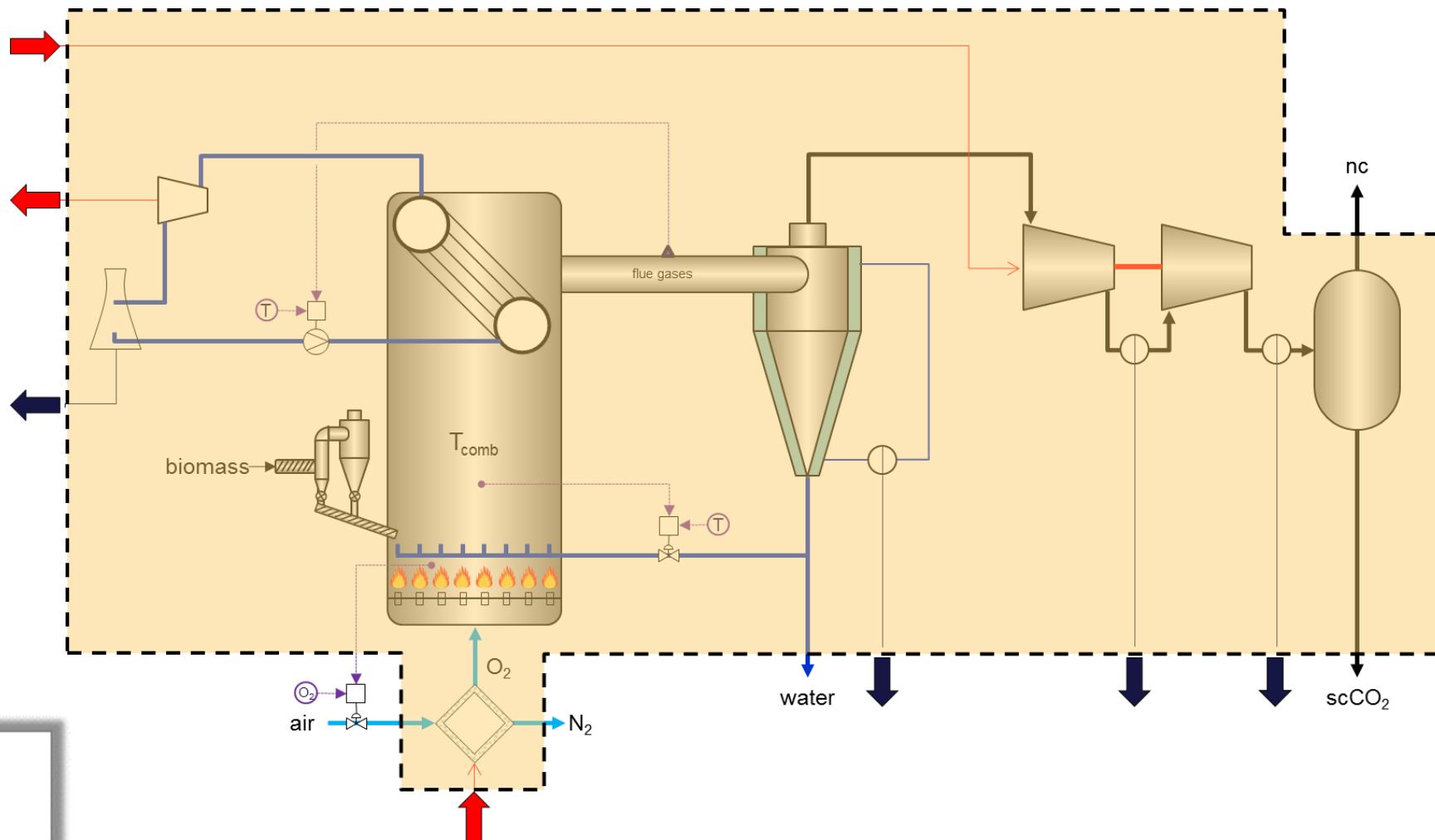
Upload

Pesquisar na Web e no Windows

14:41

13/06/2016

# Próxima Aula...



Análise exergética de uma caldeira de oxicombustão de biomassa...

# Análise Exerg

$$\frac{Q_{vc}}{n_E} - \frac{W_{vc}}{n_E} = [8 \cdot (h_f^0 + \Delta h)_{CO_2}$$

$$h_{f,C_8H_{18}(\text{liq})}^0 = -249.910 \text{ kJ/mol}$$

$$h_{f,\text{CO}_2(\text{g})}^0 = -393.520 \text{ kJ/mol}$$

$$h_{f,\text{H}_2\text{O}(g)}^0 = -241.820 \text{ kJ/mol}$$

**TABLE A-25** Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, <i>M</i> (kg/kmol)	Enthalpy of Formation, $\bar{H}_f^\circ$ (kJ/kmol)	Gibbs Function of Formation, $\bar{G}_f^\circ$ (kJ/kmol)	Absolute Entropy, $\bar{s}^\circ$ (kJ/kmol · K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H <sub>2</sub> (g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N <sub>2</sub> (g)	28.01	0	0	191.50	—	—
Oxygen	O <sub>2</sub> (g)	32.00	0	0	205.03	—	—
Carbon monoxide	CO(g)	28.01	-110,530	-137,150	197.54	—	—
Carbon dioxide	CO <sub>2</sub> (g)	44.01	-393,520	-394,380	213.69	—	—
Water	H <sub>2</sub> O(g)	18.02	-241,820	-228,590	188.72	—	—
Water	H <sub>2</sub> O(l)	18.02	-285,830	-237,180	69.95	—	—
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub> (g)	34.02	-136,310	-105,600	232.63	—	—
Ammonia	NH <sub>3</sub> (g)	17.03	-46,190	-16,590	192.33	—	—
Oxygen	O(g)	16.00	249,170	231,770	160.95	—	—
Hydrogen	H(g)	1.008	218,000	203,290	114.61	—	—
Nitrogen	N(g)	14.01	472,680	455,510	153.19	—	—
Hydroxyl	OH(g)	17.01	39,460	34,280	183.75	—	—
Methane	CH <sub>4</sub> (g)	16.04	-74,850	-50,790	186.16	55,510	50,020
Acetylene	C <sub>2</sub> H <sub>2</sub> (g)	26.04	226,730	209,170	200.85	49,910	48,220
Ethylene	C <sub>2</sub> H <sub>2</sub> (g)	28.05	52,280	68,120	219.83	50,300	47,160
Ethane	C <sub>2</sub> H <sub>6</sub> (g)	30.07	-84,680	-32,890	229.49	51,870	47,480
Propylene	C <sub>3</sub> H <sub>6</sub> (g)	42.08	20,410	62,720	266.94	48,920	45,780
Propane	C <sub>3</sub> H <sub>8</sub> (g)	44.09	-103,850	-23,490	269.91	50,350	46,360
Butane	C <sub>4</sub> H <sub>10</sub> (g)	58.12	-126,150	-15,710	310.03	49,500	45,720
Pentane	C <sub>5</sub> H <sub>12</sub> (g)	72.15	-146,440	-8,200	348.40	49,010	45,350
Octane	C <sub>8</sub> H <sub>18</sub> (g)	114.22	-208,450	17,320	463.67	48,260	44,790
Octane	C <sub>8</sub> H <sub>18</sub> (l)	114.22	-249,910	6,610	360.79	47,900	44,430
Benzene	C <sub>6</sub> H <sub>6</sub> (g)	78.11	82,930	129,660	269.20	42,270	40,580
Methyl alcohol	CH <sub>3</sub> OH(g)	32.04	-200,890	-162,140	239.70	23,850	21,110
Methyl alcohol	CH <sub>3</sub> OH(l)	32.04	-238,810	-166,290	126.80	22,670	19,920
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH(g)	46.07	-235,310	-168,570	282.59	30,590	27,720
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH(l)	46.07	-277,690	174,890	160.70	29,670	26,800

*Source:* Based on JANAF Thermochemical Tables, NSRDS-NBS-37, 1971; Selected Values of Chemical Thermodynamic Properties, NBS Technical Note 270-3, 1968; and API Research Project 44, Carnegie Press, 1953. Heating values calculated.

Note 270-3. 1968; and *API Research Project 44*, Carnegie Press, 1953. Heating values calculated.

Properties, NBS Tech.