Thermodynamics

- The study of the different forms of Energy and how they are transformed according to strict laws....

- It allows the knowledge of the energy given up or absorbed in a transformation as well as the spontaneity of the same.

Principles

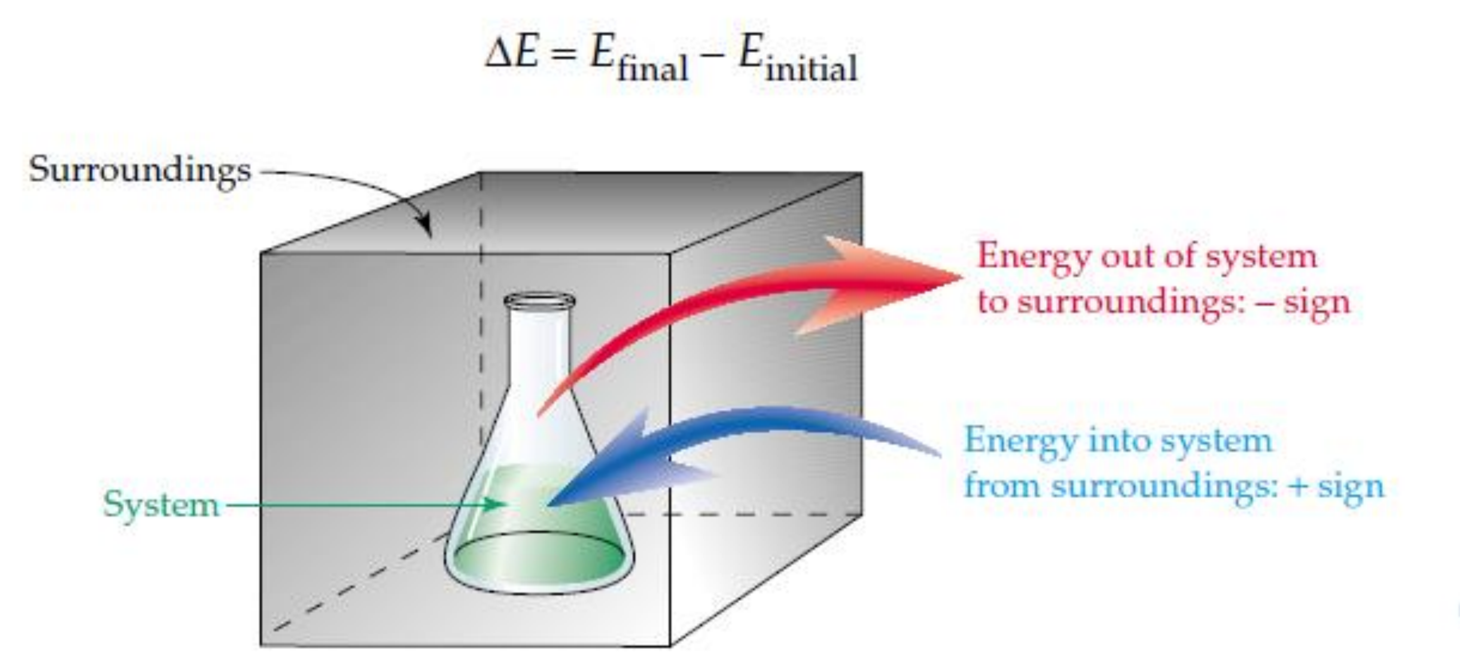
0. This principle explains the fact that two bodies at different temperatures, between which heat is exchanged, (even if this concept is not present in the zero principle) end up reaching the same temperature.

1. **Energy is not created and neither destroyed, it is transformed into different forms**
2. **Spontaneous transformations of energy always go towards forms whose dispersion (disorder -caos) is greater**
3. Nernst's theorem: "it is not possible to reach absolute zero (0 K) in a finite number of operations (thermodynamic transformations)"

A few definitions

- A **system** is a portion of real or imaginary matter/space, within which a process is observed:
- a) open, b) closed, c) insulated.
- The **surroundings** is made up of all the surrounding matter that exchanges matter or energy with the system.
- The **Universe** is the combination of system and environment.

Energy exchanges



Variables and Functions

- **Thermodynamic variables** are measurable properties of a system; they are extensive (V, m) when in a system given by the union of two systems, the variable is the sum of the corresponding original variables, otherwise the variables are intensive (T, p).
- **Thermodynamic functions** (energy values) define the state of a system. Many of these are state functions (they depend only on the initial and final state of the system)

Laws

- Energy can neither be created nor destroyed

- There are various forms of energy; the less noble and more dispersive (chaotic) ones tend to increase at the expense of the nobler ones

Some Formulas

- Internal Energy U includes all the energies contained in the matter contained within a system

$$U = E_{vib}+E_{rot}+E_{trasl}+E_{el}+\ldots\ldots$$

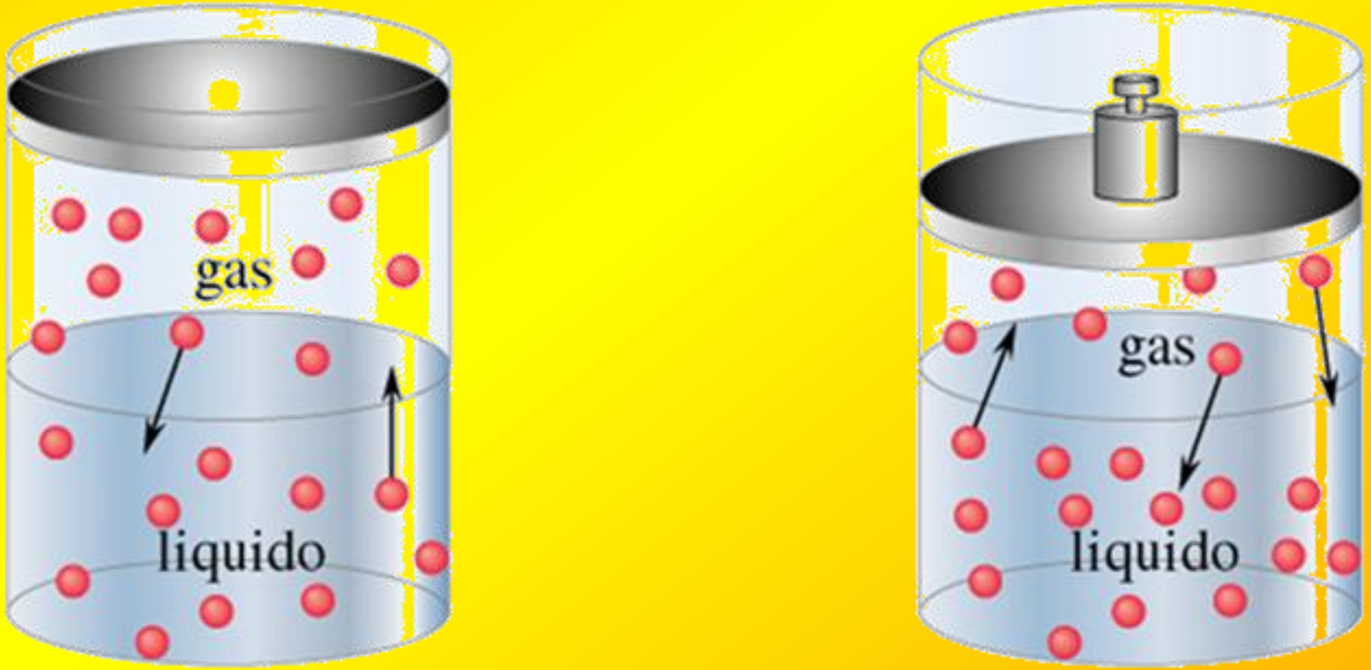
$$\Delta U = Q + W$$

- The work done by a system is given by the force exerted on the walls * the displacement of a movable wall

Work

$$W = F \cdot s \ (J = N \cdot m)$$

$$W = p/A; \ \Delta V = s \cdot A \rightarrow W = -p \cdot \Delta V$$



Pushig against a cilinder is a positive work
for the system

Enthalpy and internal energy

$$W = -p \cdot \Delta V$$

at constant atmospheric pressure

$$\Delta U = Q + L = Q_p - p \cdot \Delta V$$

Defining enthalpy as heat exchanged at constant pressure

$$\Delta H = Q_p$$

therefore

$$\Delta H = \Delta U + p \cdot \Delta V$$

Enthalpy is the thermodynamic state function that is easily measured in the laboratory and then used to characterize reactions

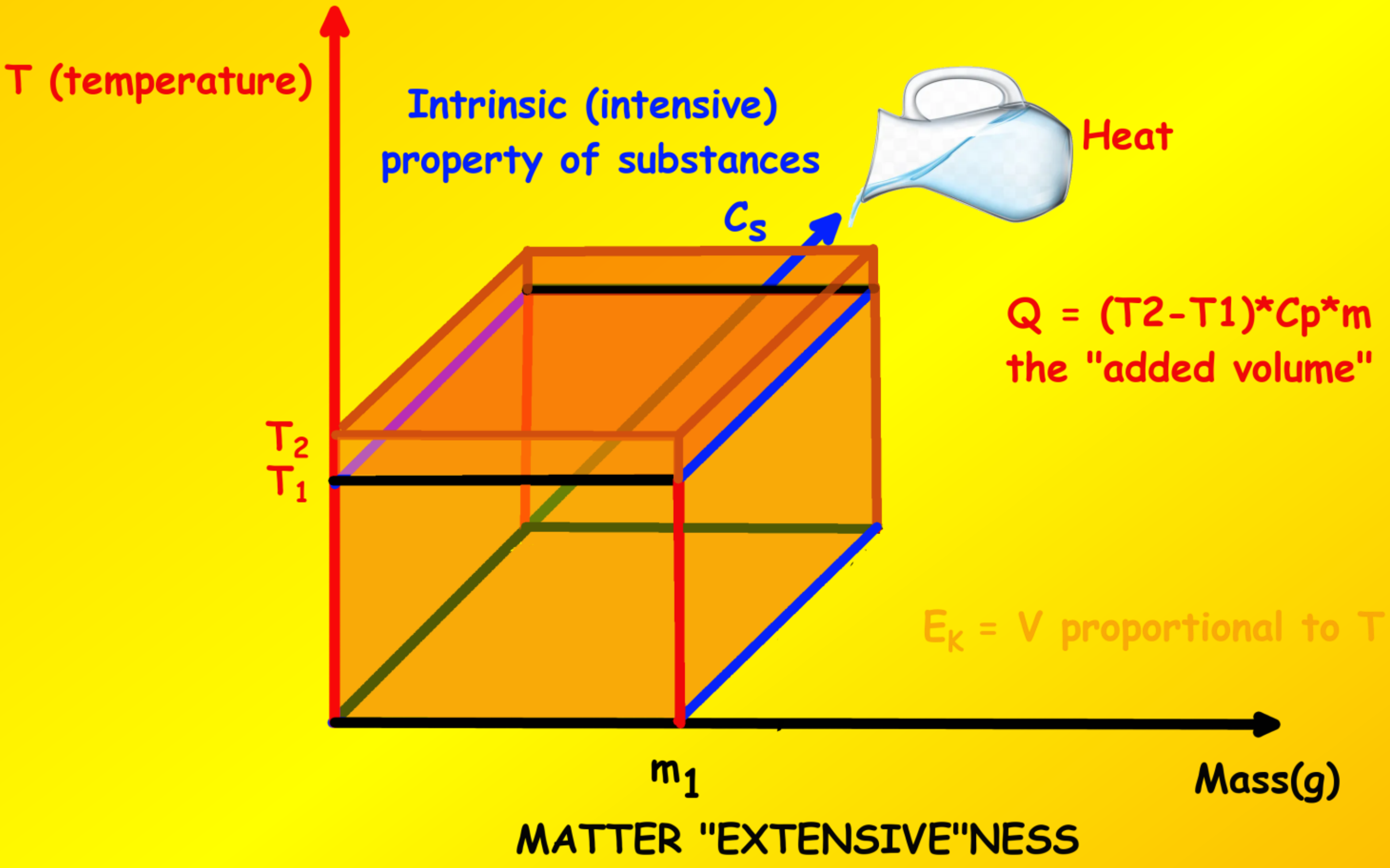
Heat

- A less noble form of energy that can be detected by temperature variations that also depend on the matter under examination (by means of a quantity known as heat capacity)

$$Q = C \cdot \Delta T$$

- The SI unit of measurement is the Joule, but the Cal is very common

$$1\text{cal} = 4.18\ \text{J}$$

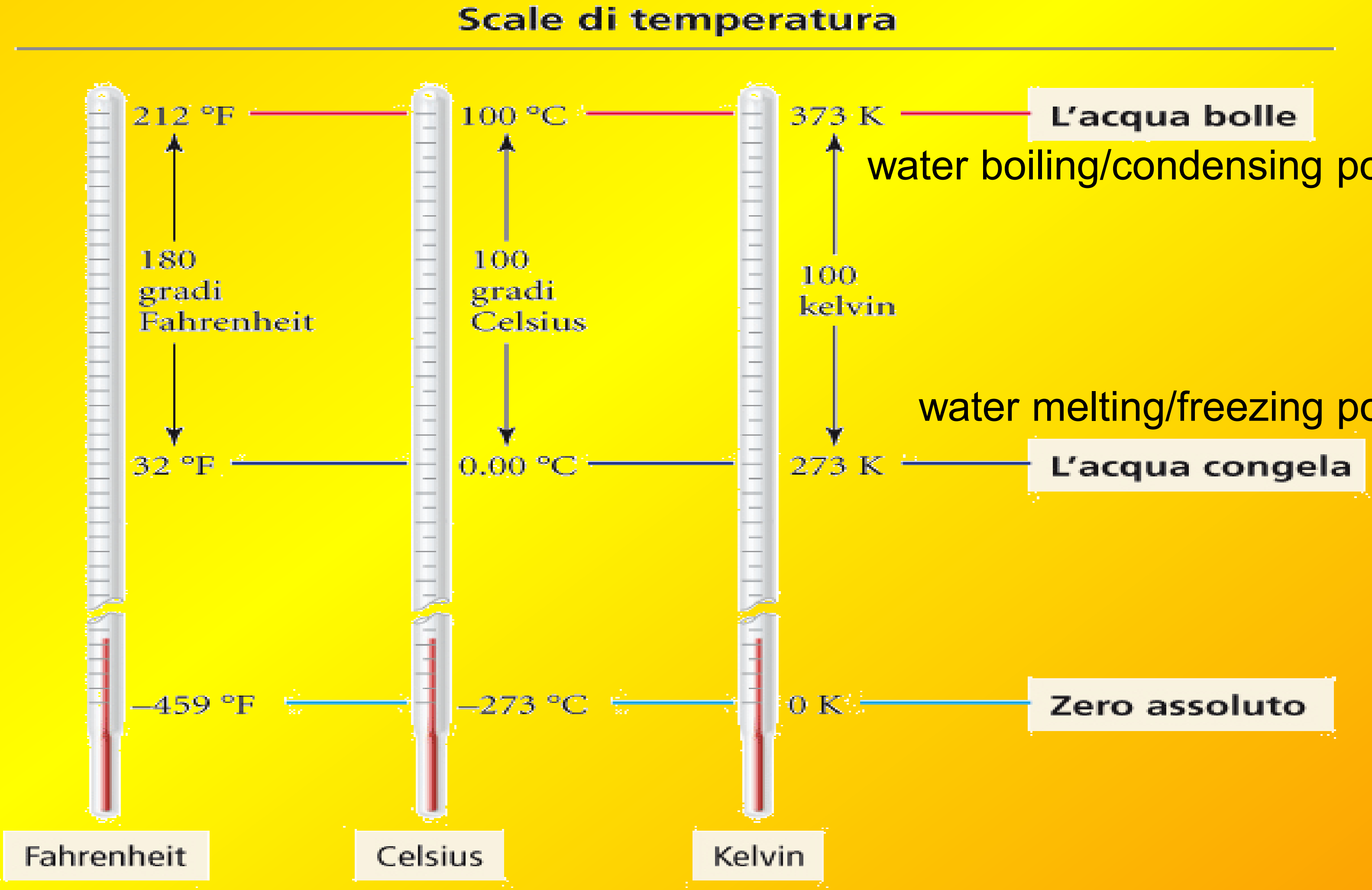


Q = (T2-T1)*Cp*m

the "added volume"

E_K = V proportional to T

Temperature Scales



water boiling/condensing point

water melting/freezing point

Caos

- The second principle dictates that universal chaos (better dispersion) increases, numerically, the thermodynamic variable that identifies chaos is entropy S.

Statistics $\Delta S = S_2 - S_1 = k \ln w_2/w_1$

Thermodynamics $\Delta S = \underline{Q_{REV}/T}$

$$\underline{\Delta S_{UN} = \Delta S_{SIST} + \Delta S_{AMB} > 0}$$

Entropy Representation

AMBIENTE ORDINATO
TEMPERATURA BASSA

piccolo numero
di microstati
suscettibili di
crescita
esponenziale

GRANDE AUMENTO
DI ENTROPIA
$\Delta S = Q/T$ ALTO

CALORE = Q

AMBIENTE DISORDINATO
TEMPERATURA ALTA

numero di
microstati
già grande
che può essere
aumentato di poco

LIMITATO AUMENTO
DI ENTROPIA
$\Delta S = Q/T$ BASSO

Spontaneity of processes
Gibbs Energy

$$\Delta S_{UN} = \Delta S_{SIST} + \Delta S_{AMB}$$

$$\Delta S_{UN} = \Delta S_{SIST} - \Delta H_{SIST}/T$$

$$-T\,\Delta S_{UN} = \Delta H_{SIST} - T\Delta S_{SIST}$$

$$\mathbf{\Delta G = \Delta H_{SIST} - T\,\Delta S_{SIST} < 0}$$

$$T\Delta S_{UN}^{\circ} = \Delta G^{\circ} = -RT\ln K_c$$

Reazioni spontanee $\Delta G < 0$ $(\Delta S_{UN} > 0)$

Reazioni non spontanee $\Delta G > 0$ $(\Delta S_{UN} < 0)$

Reazioni all'equilibrio $\Delta G = 0$ $(\Delta S_{UN} = 0)$

$-\Delta H_{SYS} \rightarrow \frac{Q_{RE}}{T}$

$\Delta S_{UN} > 0$

$\Delta S_{UN} = \Delta S_{SYS} + \Delta S_{SUR}$

$\Delta S_{SYS} - \frac{\Delta H_{SYS}}{T} > 0$

$\Delta G = -T \cdot \Delta S_{UN} < 0$

$\Delta G = +\Delta H_{SYS} - T\Delta S_{SYS}$

GIBBS

- If nature does not answer first what we want, it is better to take what answer we get. -- Josiah Willard Gibbs, Lecture XXX, Monday, February 5, 1900

$\Delta H < 0$ $\Delta G < 0$

Exothermy and Spontaneity

- Spontaneous exothermic reactions (the majority)
- $\Delta G<0$; $\Delta H<0$

$$\Delta G = \Delta H - T\Delta S$$

- Spontaneous endothermic reactions (rare cases)
- $\Delta G<0$; $\Delta H>0$; therefore $\Delta S>>0$

$\Delta G < 0$ $\Delta H > 0$ $T\Delta S > \Delta H$

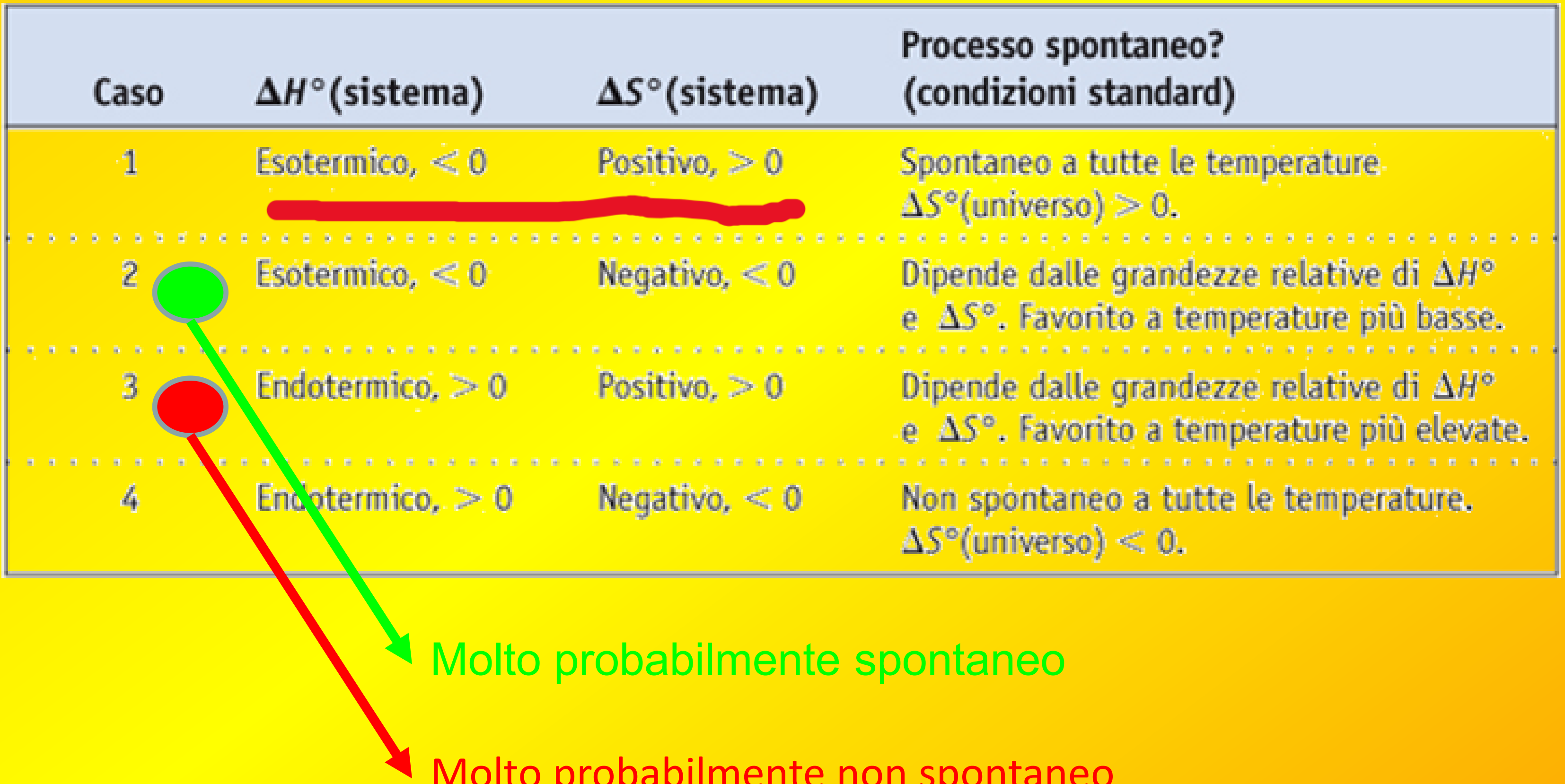
Exothermic-Endothermic and Exergonic and Endoergonic

Exothermic = indicate a reaction releasing heat into the surroundings (at constant p), decreasing the total energy of the system

Endothermic = refers to a reaction absorbing heat from the surroundings, increasing the total energy of the system

Exergonic indicates a chemical reaction that releases free energy making it spontaneous

General Scheme



Caso	$\Delta H°$(sistema)	$\Delta S°$(sistema)	Processo spontaneo? (condizioni standard)
1	Esotermico, < 0	Positivo, > 0	Spontaneo a tutte le temperature $\Delta S°$(universo) > 0.
2	Esotermico, < 0	Negativo, < 0	Dipende dalle grandezze relative di $\Delta H°$ e $\Delta S°$. Favorito a temperature più basse.
3	Endotermico, > 0	Positivo, > 0	Dipende dalle grandezze relative di $\Delta H°$ e $\Delta S°$. Favorito a temperature più elevate.
4	Endotermico, > 0	Negativo, < 0	Non spontaneo a tutte le temperature. $\Delta S°$(universo) < 0.

Molto probabilmente spontaneo

Molto probabilmente non spontaneo

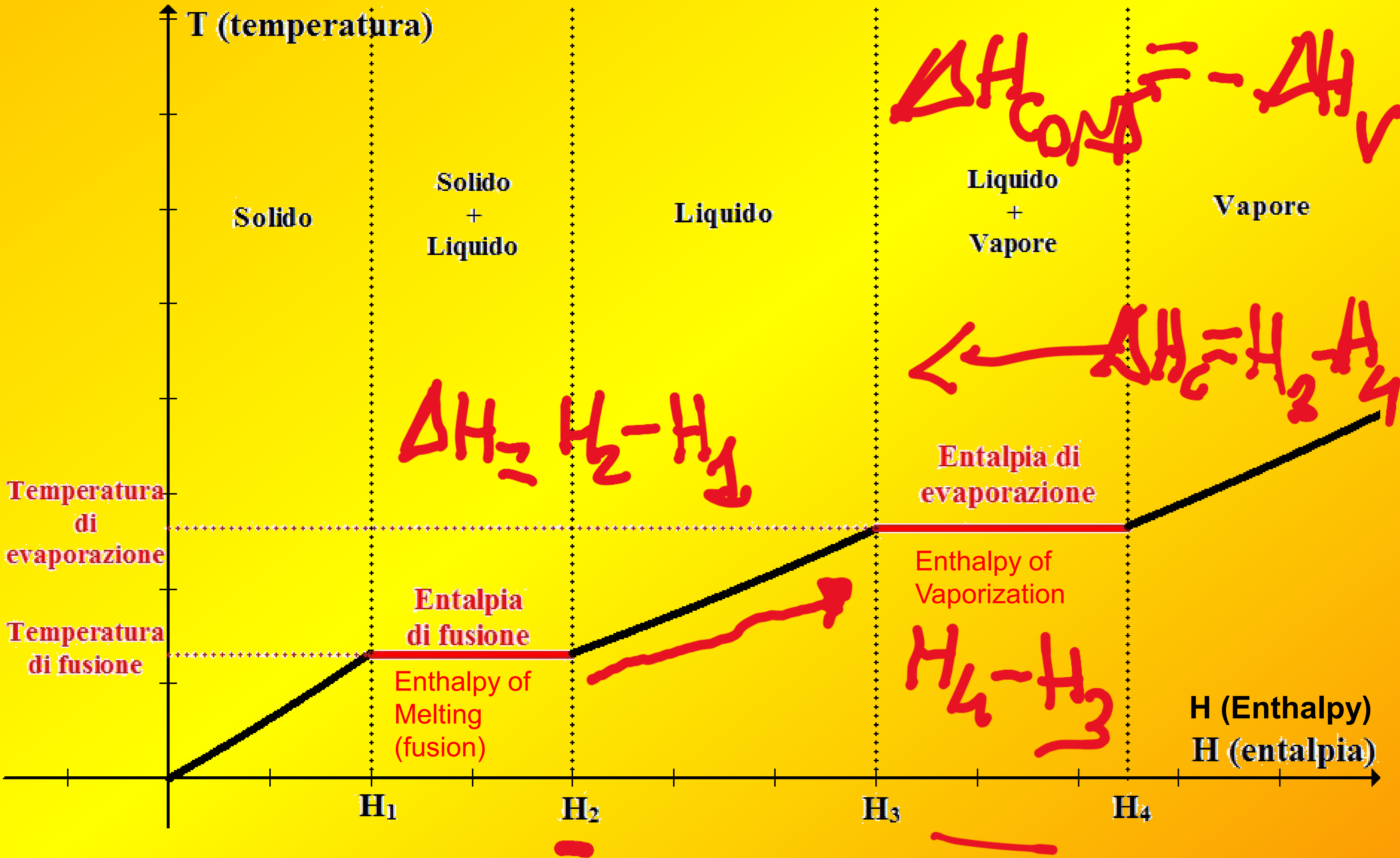
Photosynthesis

$$\underline{6H_2O(l) + 6CO_2(g)} \rightarrow \underline{C_6H_{12}O_6(s)} + 6O_2(g)$$

$\Delta H^\circ = +2800 kJ/mol$!!!

Only plants can do this, but with difficulty: thanks to a protein known as chlorophyll, they convey the energy of photons to make this process take place NOT spontaneously

Enthalpy and state transitions



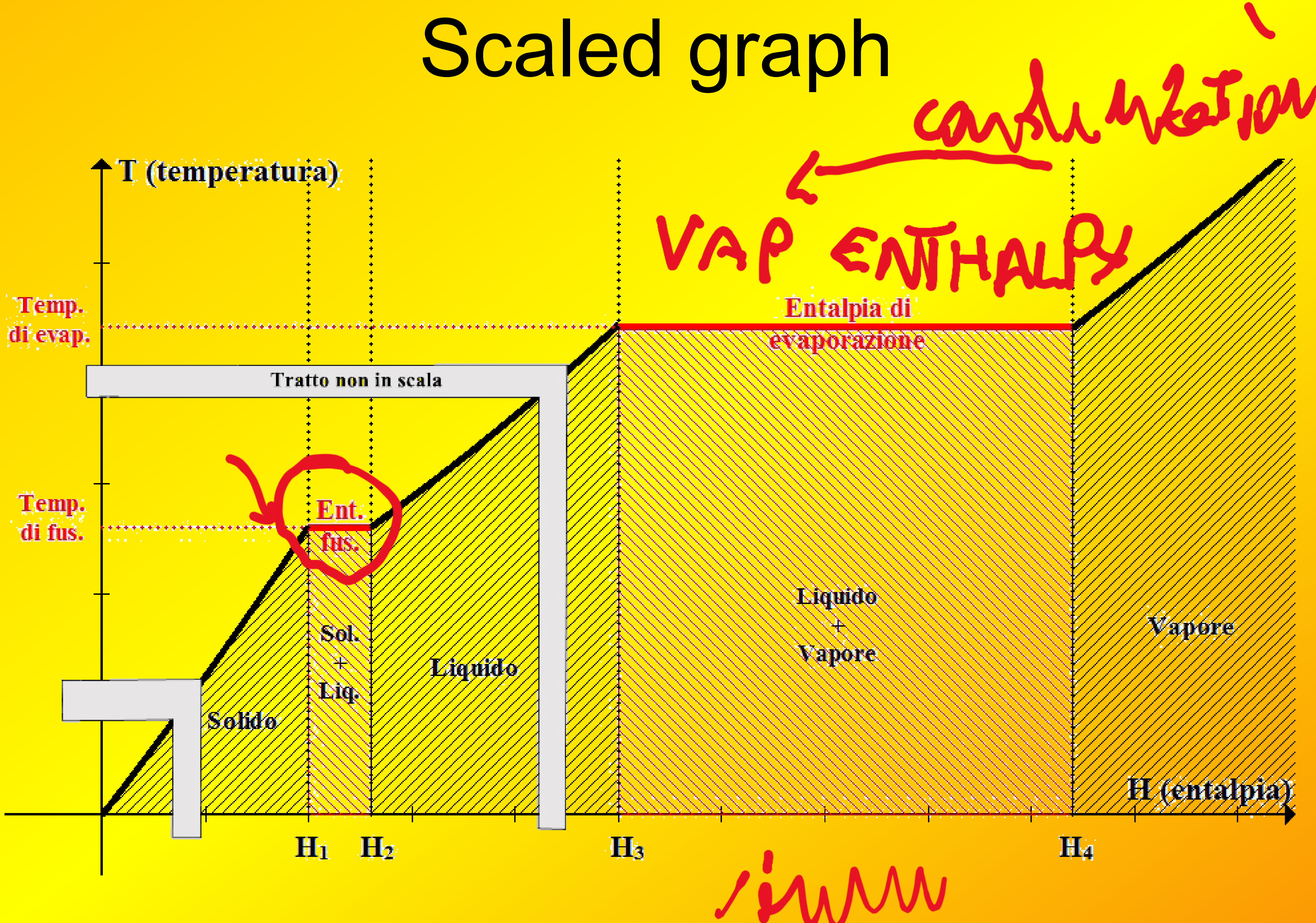
$\Delta H_{cond} = -\Delta H_v$

$\Delta H_c = H_3 - H_4$

$\Delta H = H_2 - H_1$

$H_4 - H_3$

Scaled graph



Hess's Law

$A \rightarrow B \quad \Delta H^\circ_1$

$B \rightarrow C \quad \Delta H^\circ_2$

$C \rightarrow D \quad \Delta H^\circ_3$

$A \rightarrow D \quad \underline{\Delta H^\circ}_{TOT} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$

O_2, H_2

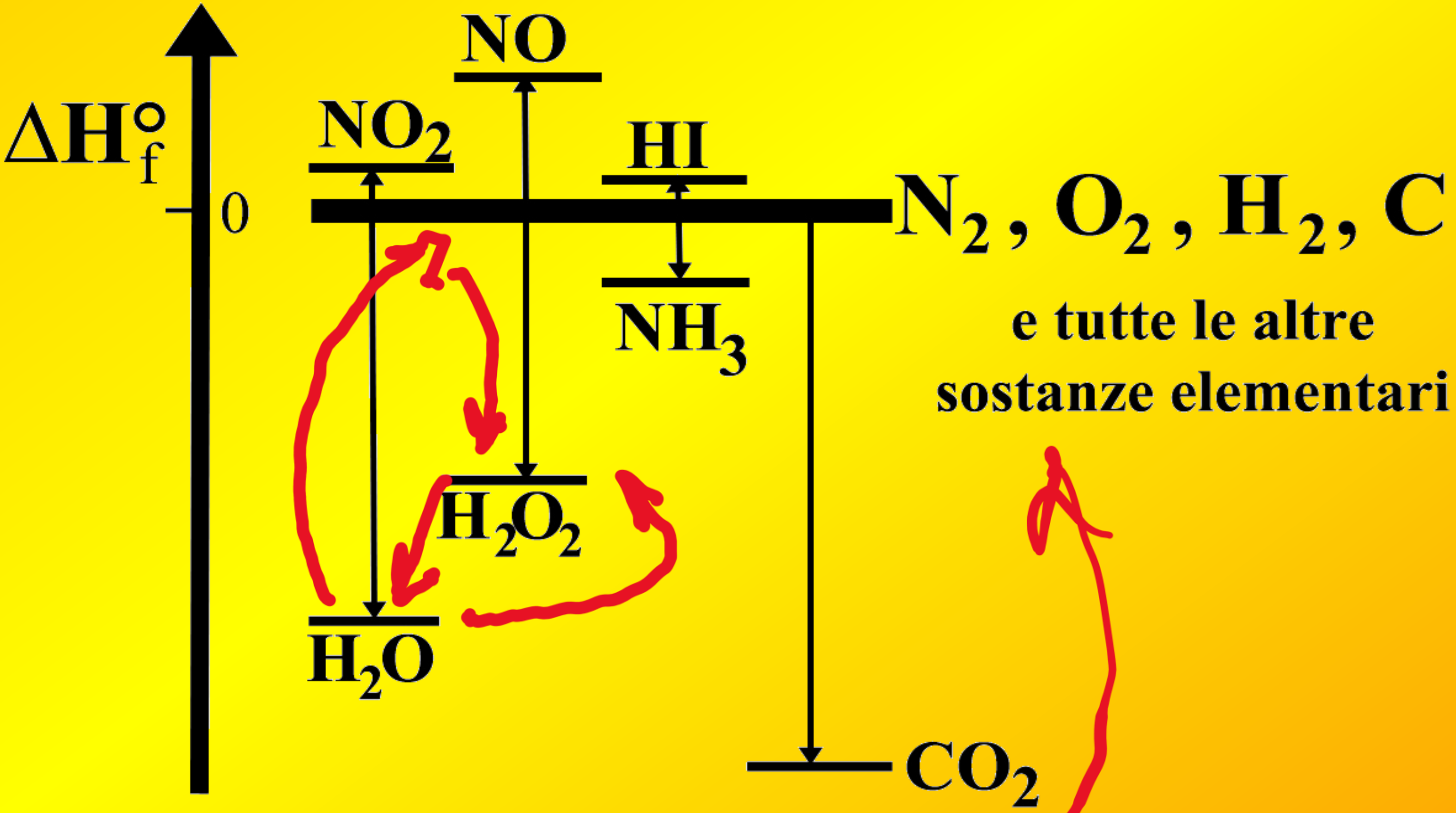
Enthalpy of formation

298K 25°C
1ATM

✓

Sostanza	ΔH°$_f$ (kJ/mol)
✗ H_2O(l)	-285.83
H_2O_2(l)	-187.8
NH_3(g)	-46.11
NO(g)	90.25
NO_2(g)	33.2
SO_2(g)	-296.8
HCl(g)	-92.31
HI(g)	26.5
✗ CO_2(g)	-393.51

Reference
Enthalpy of Formation



$2H_2O_2 \rightarrow 2H_2O + O_2$

$\Delta H^\circ_r = \Sigma\, \Delta H^\circ_f$ (products) - $\Sigma\, \Delta H^\circ_f$ (reagents)

All related to elements in the standard state

$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(g)}$

a) PRODOTTI = 1) $N_2O_{(g)}$ $\Delta H^\circ_f = +82$ kJ/mol x 1 = + 82 kJ/mol

2) $H_2O_{(g)}$ $\Delta H^\circ_f = -242$ kJ/mol x 2 = - 484 kJ/mol

$\Sigma\, \Delta H^\circ_f$ (PRODOTTI) = - 484 + 82 = - 402kJ/mol

b) REAGENTI = 1) $NH_4NO_{3(s)}$ $\Delta H^\circ_f = -366$kJ/mol;

$\Sigma\, \Delta H^\circ_f$ (REAGENTI) = -366 kJ/mol

eseguendo quindi la differenza tra le due sommatorie si ottiene il ΔH° della reazione:

$$\Delta H^\circ_r = \underset{\uparrow}{-402} \quad - \quad \underset{\uparrow}{(-366)} = \quad -36 \text{ kJ/mol}$$

$$\Delta H^\circ_r = \quad \Sigma\, \Delta H^\circ_f \text{ (PRODOTTI)} \quad - \quad \Sigma\, \Delta H^\circ_f \text{ (REAGENTI)}$$

$\Delta H^\circ_r = \Sigma\, \Delta H^\circ_c$ (reagents) - $\Sigma\, \Delta H^\circ_c$ (products)

All related to totally oxidised elements in the standard state

OKIDISES

Per cui il ΔH°_f del metano può essere calcolato dai calori di combustione mediante la combinazione algebrica: $\Delta H^\circ_2 + 2 \times \Delta H^\circ_3 - \Delta H^\circ_1$, numericamente:

$\Delta H^\circ_f = (-393 - 286 \times 2) - (-890) = -75$ kJ mol^{-1}.

Eseguiamo il medesimo procedimento per il calcolo del ΔH°_f del glucosio $C_6H_{12}O_6$:

(1) $C_6H_{12}O_{6(s)} + 6\ O_{2\ (g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$; $\Delta H^\circ_1 = -2803$ kJmol^{-1}

(2) $C_{(graf)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H^\circ_2 = -393$ kJ mol^{-1}

(3) $H_{2(g)} + \frac{1}{2}\ O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H^\circ_3 = -286$ kJ mol^{-1}

La reazione di formazione può essere ottenuta dalla combinazione (2)x6 + (3)x6 – (1) per cui: $\Delta H^\circ_f = (-393 \times 6 - 286 \times 6) - (-2803) = -1271$ kJ mol^{-1}.

$6C_{(graf)} + 6\ H_{2(g)} + 3\ O_{2(g)} \longrightarrow C_6H_{12}O_{6(s)}$; $\Delta H^\circ_f = -1271$ kJ mol^{-1}

ESERCIZIO: Si calcoli il ΔH°_f del propano C_3H_8 sapendo che il ΔH° di combustione di questo idrocarburo è -2220 kJ mol^{-1}. Per i ΔH° di combustione di $H_{2(g)}$ e $C_{(graf)}$ vedere i precedenti calcoli.

$E = h\nu$

ENERGY

Ionization potential

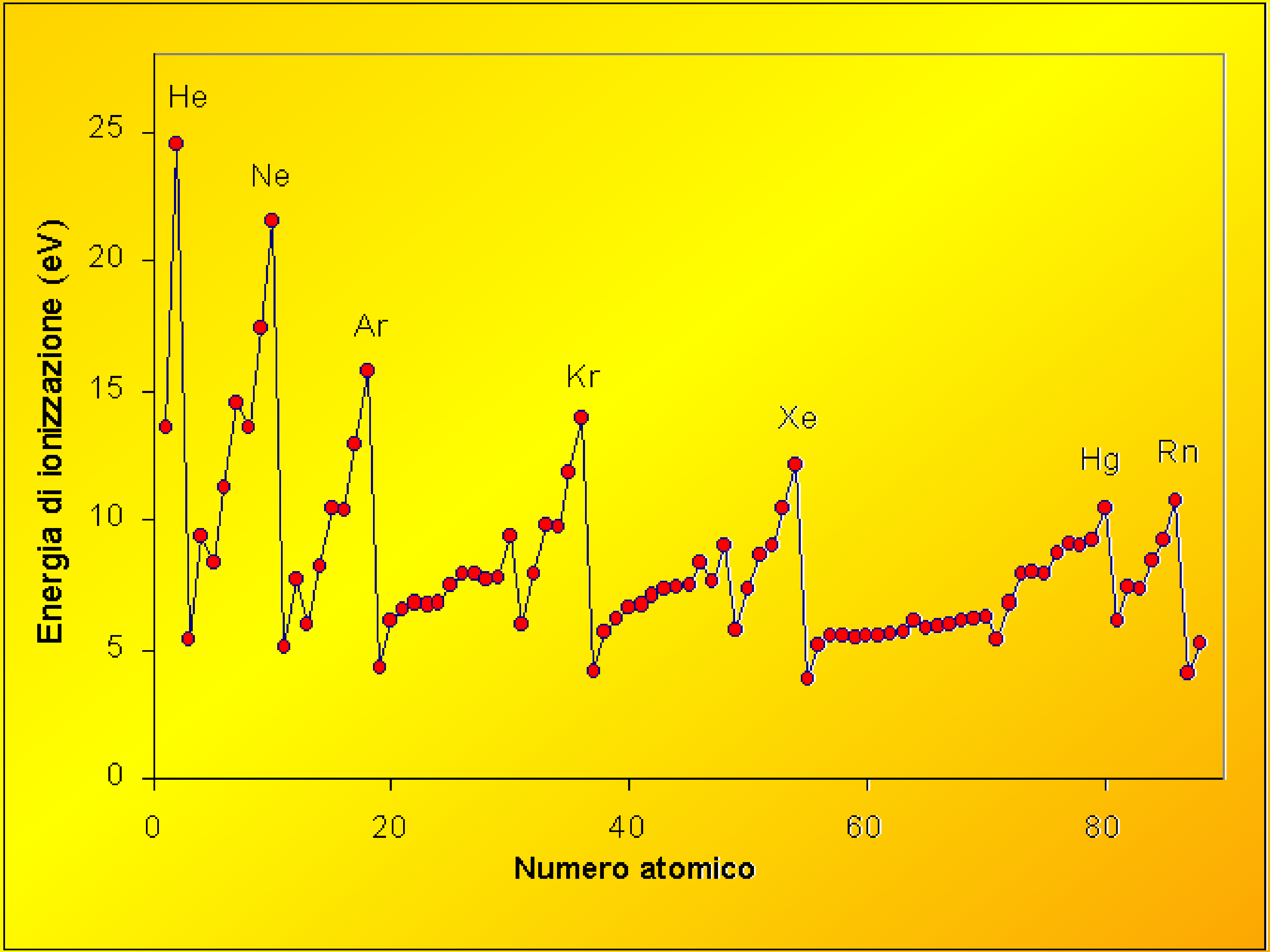
- A → $A^+ + e^-$ $\Delta H°$ sempre >0.

× mol

- Mg → $Mg^+ + e^-$ $PI_I = 738$ kJ/mol
- Mg^+ → $Mg^{2+} + e^-$ $PI_{II} = 1451$ kJ/mol
- Na → $Na^+ + e^-$ $PI_I = 496$ kJ/mol
- Na^+ → $Na^{2+} + e^-$ $PI_{II} = 4562$ kJ/mol

$2s^2p^6 \rightarrow 2s^2p^5$

Configurazioni elettroniche stabili

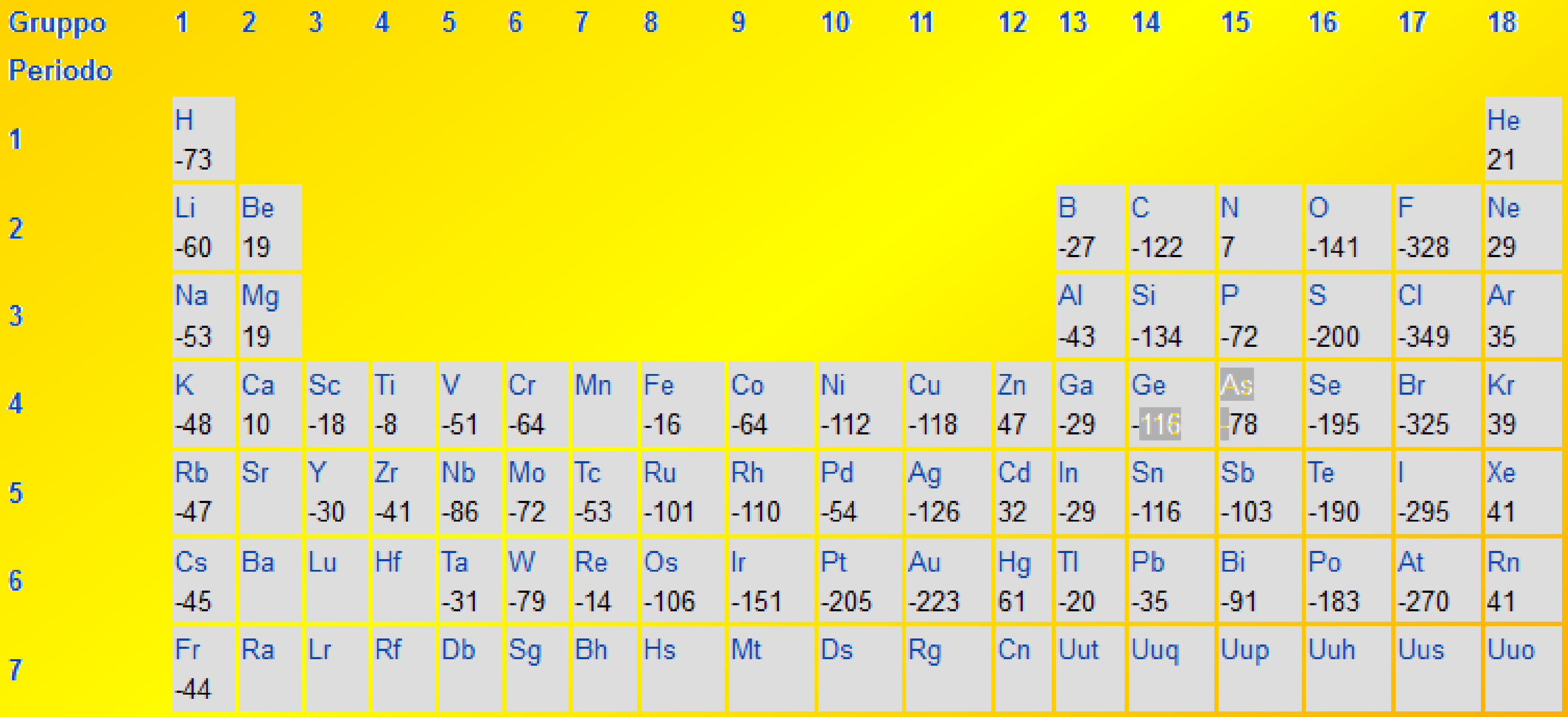


Electron Affinity

$F + e^- \rightarrow F^-$

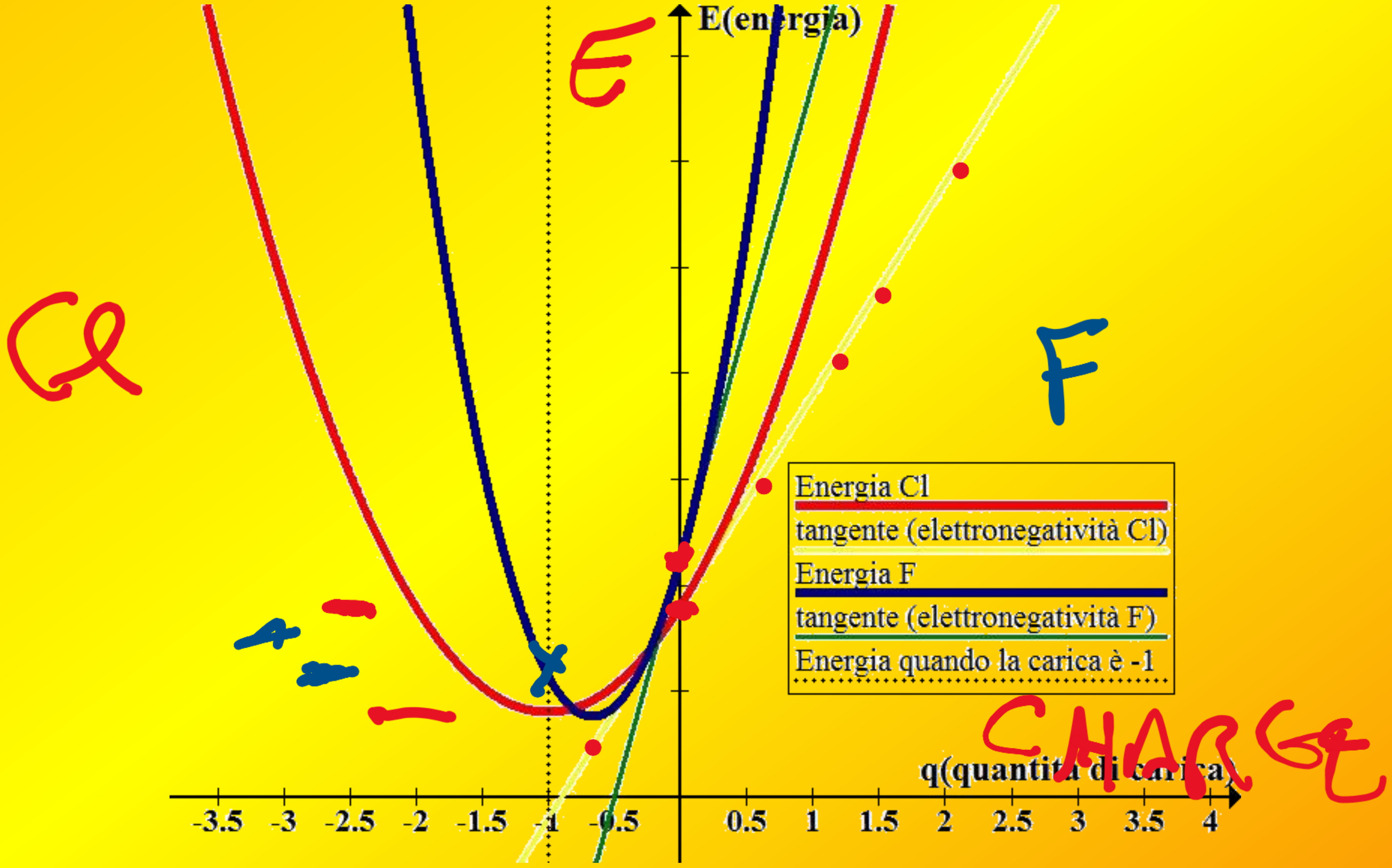
$\Delta H^\circ = -328\ kJ/mol \Rightarrow A.E. = 328\ kJ/mol$

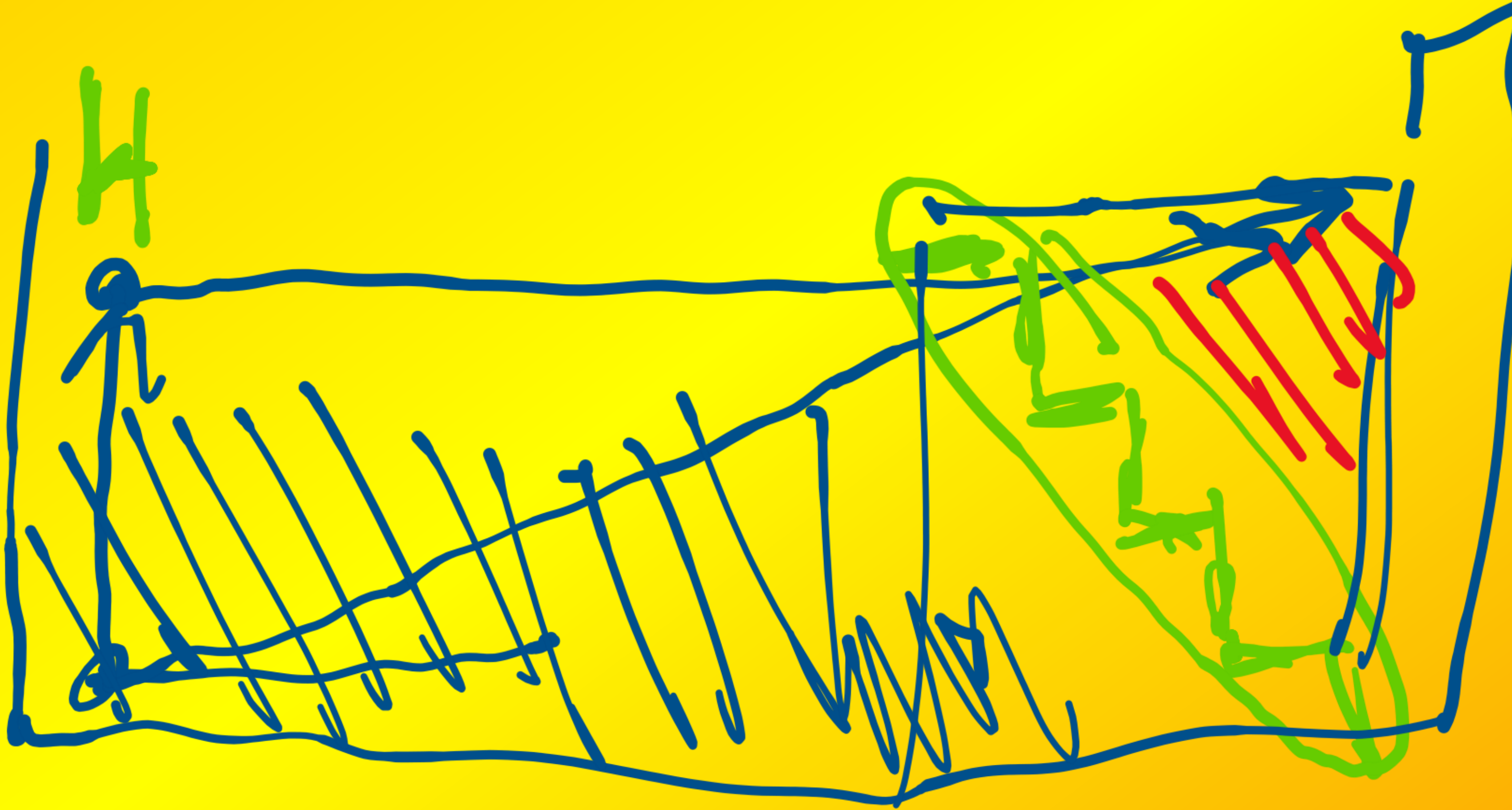
Energies for the addition of an electron



Gruppo Periodo	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H -73																	He 21
2	Li -60	Be 19											B -27	C -122	N 7	O -141	F -328	Ne 29
3	Na -53	Mg 19											Al -43	Si -134	P -72	S -200	Cl -349	Ar 35
4	K -48	Ca 10	Sc -18	Ti -8	V -51	Cr -64	Mn	Fe -16	Co -64	Ni -112	Cu -118	Zn 47	Ga -29	Ge -116	As -78	Se -195	Br -325	Kr 39
5	Rb -47	Sr	Y -30	Zr -41	Nb -86	Mo -72	Tc -53	Ru -101	Rh -110	Pd -54	Ag -126	Cd 32	In -29	Sn -116	Sb -103	Te -190	I -295	Xe 41
6	Cs -45	Ba	Lu	Hf	Ta -31	W -79	Re -14	Os -106	Ir -151	Pt -205	Au -223	Hg 61	Tl -20	Pb -35	Bi -91	Po -183	At -270	Rn 41
7	Fr -44	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

Electronegativity




H

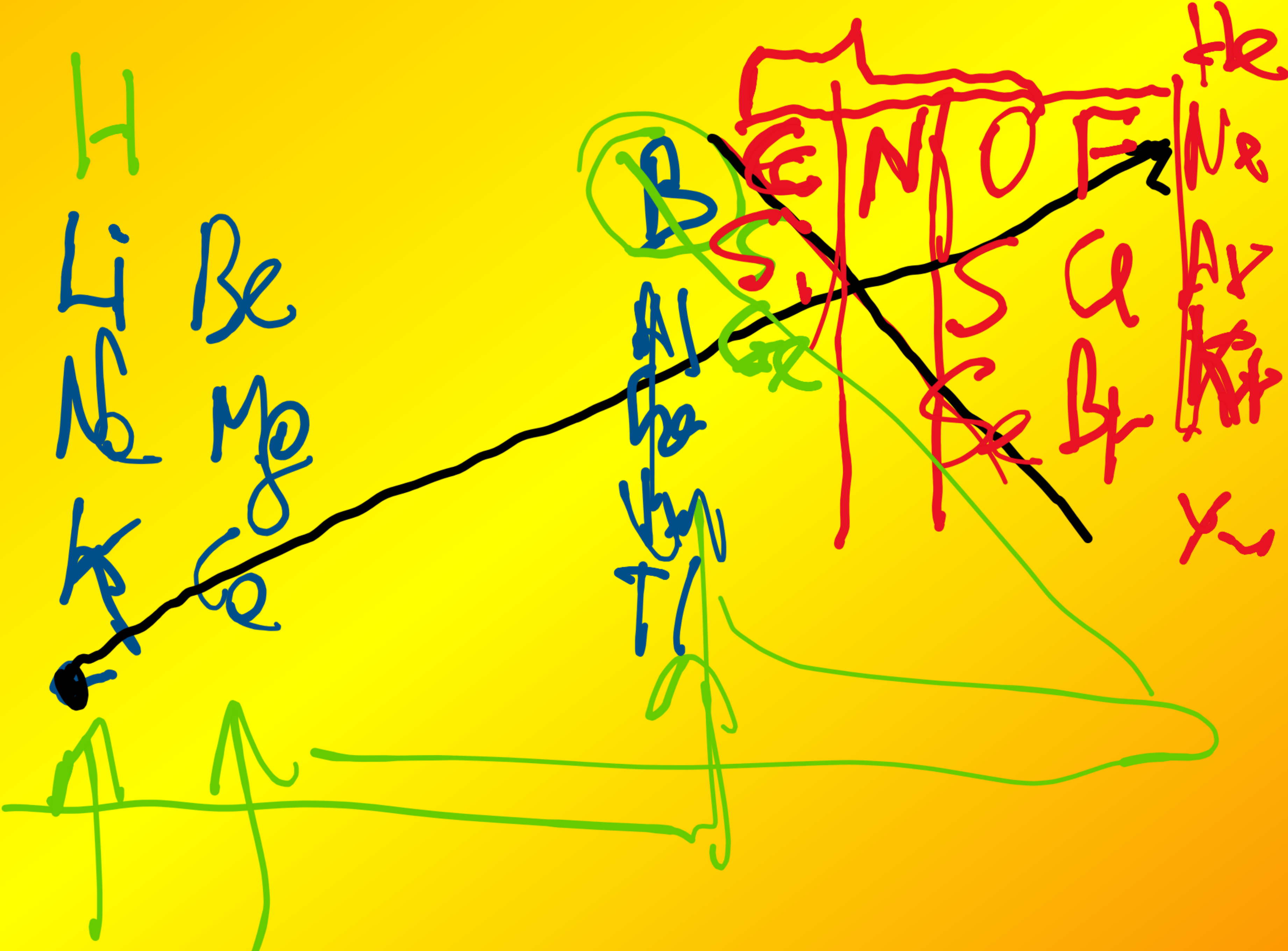
F = 4

O = 3,7

Cl = 3.6 N = 3,6

Na = 0,9

H = 2.1


H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
S
Cl
Ar
K
Ca
Ga
In
Tl
Se
Br
Kr
Xe

General Laws to Find ΔH°_r according to Hess

$$\Delta H^\circ_r = \Sigma\, \underline{\Delta H^\circ}_{f\ (PRODUCTS)} - \Sigma\, \Delta H^\circ_{f\ (REAGENTS)}$$

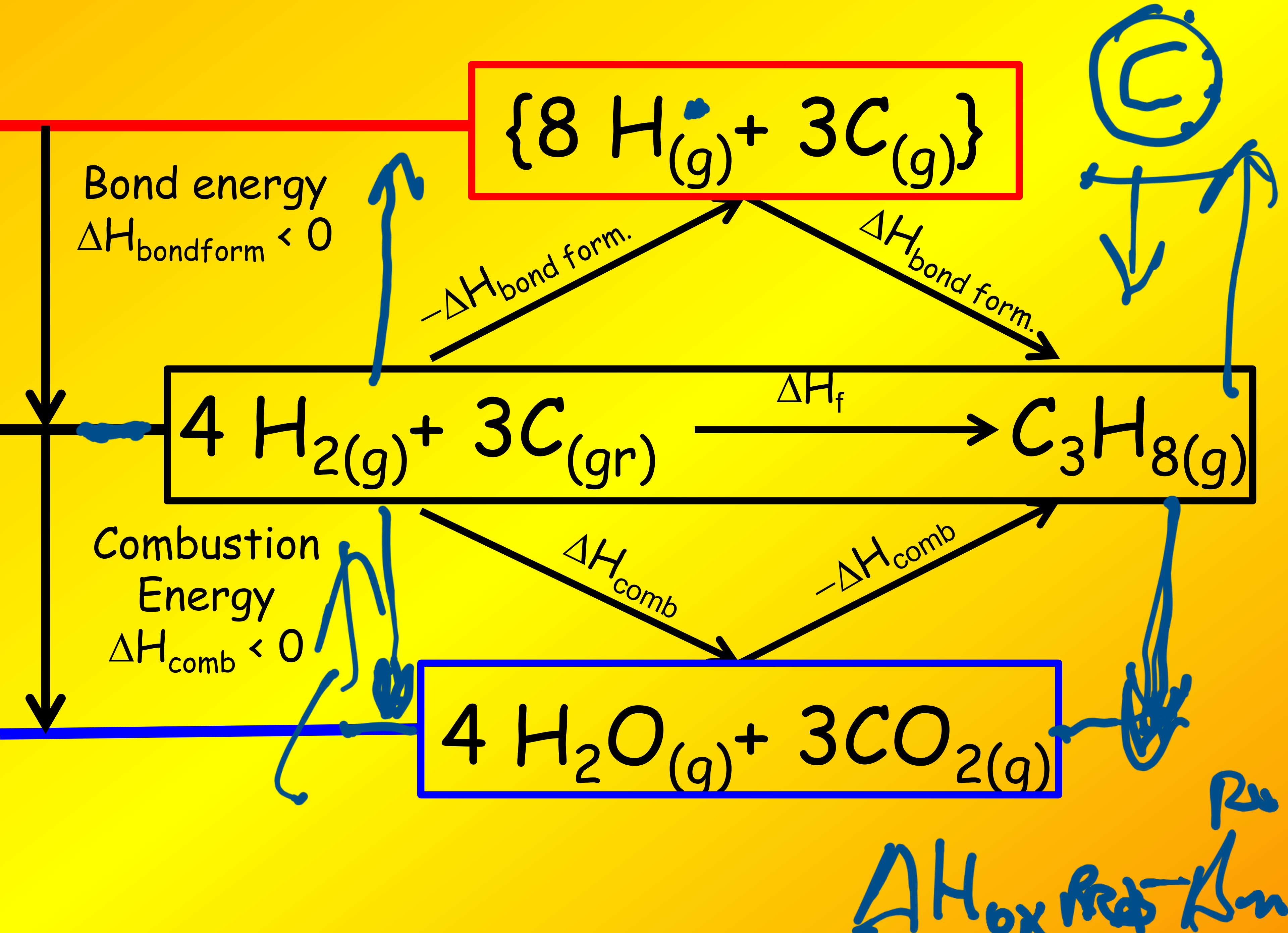
All related to items in the standard state

$$\Delta H^\circ_r = \Sigma\, \Delta H^\circ_{comb\ \underline{(REAGENTS)}} - \Sigma\, \Delta H^\circ_{comb\ (PRODUCTS)}$$

All related to combustion products in the standard state

$$\Delta H^\circ_r = \Sigma\, \underline{\Delta H^\circ_{bond\ (REAG)}} - \Sigma\, \Delta H^\circ_{bond\ (PROD)}$$

All related to the elements that make up reagents and products in the standard state



$\{8\ H_{(g)} + 3C_{(g)}\}$

Bond energy

$\Delta H_{bondform} < 0$

$-\Delta H_{bond\ form.}$

$\Delta H_{bond\ form.}$

$4\ H_{2(g)} + 3C_{(gr)} \xrightarrow{\Delta H_f} C_3H_{8(g)}$

Combustion Energy

$\Delta H_{comb} < 0$

ΔH_{comb}

$-\Delta H_{comb}$

$4\ H_2O_{(g)} + 3CO_{2(g)}$

Rx

ΔH_{ox} Prods $- \Delta$