X SCUOLA NAZIONALE DI DIDATTICA DELLA CHIMICA "GIUSEPPE DEL RE"

Discutere, Sperimentare, Riflettere. Le reazioni chimiche: il tempo e non solo

Rimini, 15 – 17 settembre 2025

"Termodinamica e cinetica, due ambiti complementari: dal possibile al reale, il ruolo chiave della variabile tempo"

Università degli Studi di Messina

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Società Chimica Italiana
Divisione di Didattica Chimica

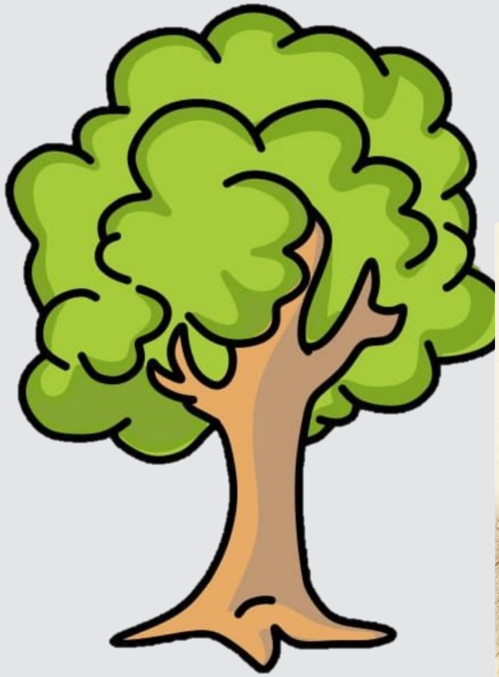
ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA | DIPARTIMENTO DI CHIMICA "GIACOMO CIAMICIAN"

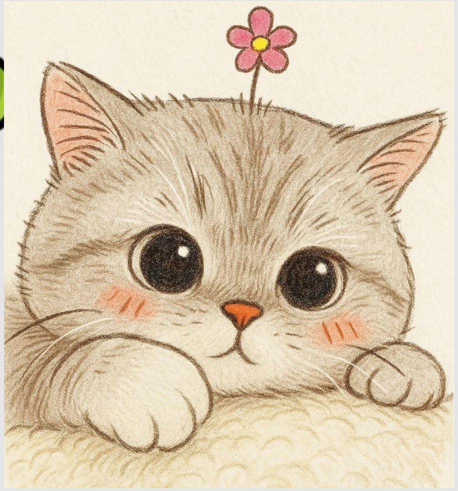
Piano Nazionale Lauree Scientifiche

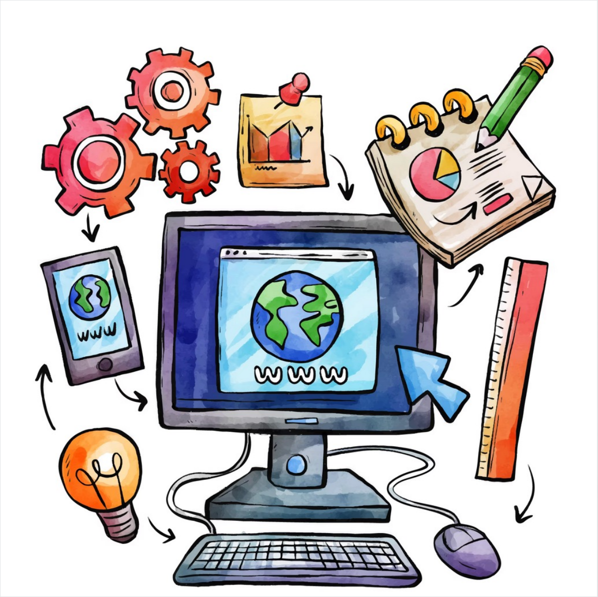
Società Chimica Italiana
Sezione Emilia Romagna

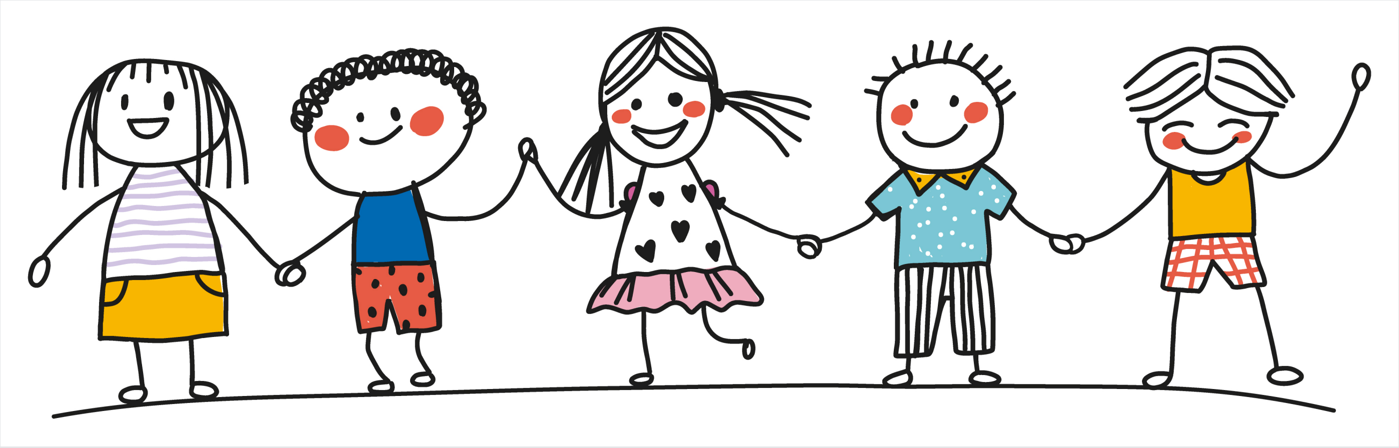
La Chimica studia la **materia** e le sue **trasformazioni**

la **materia**

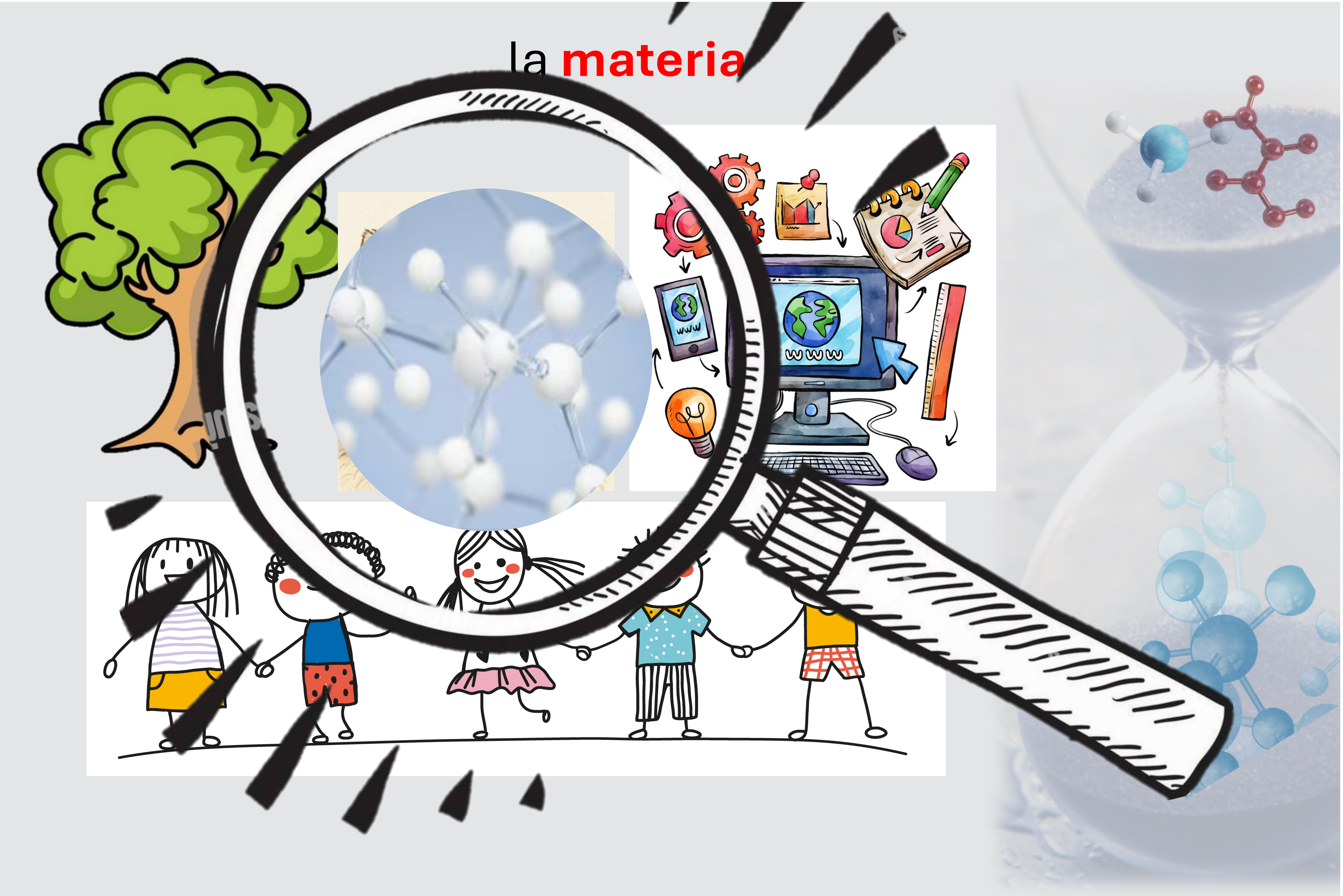




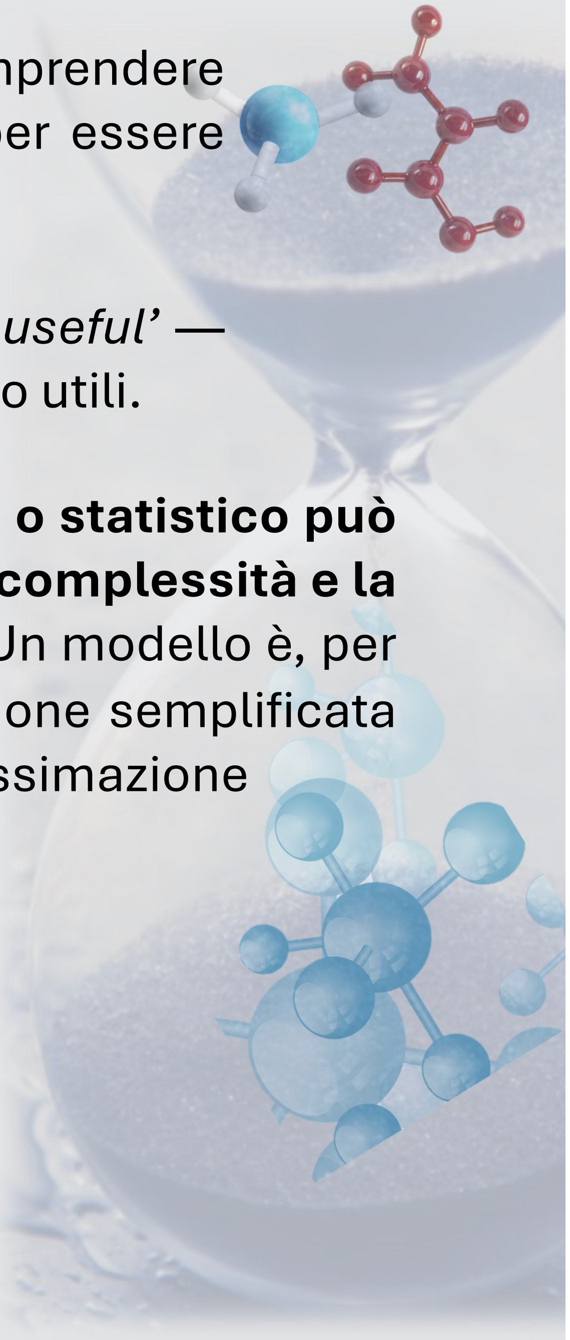




la **materia**



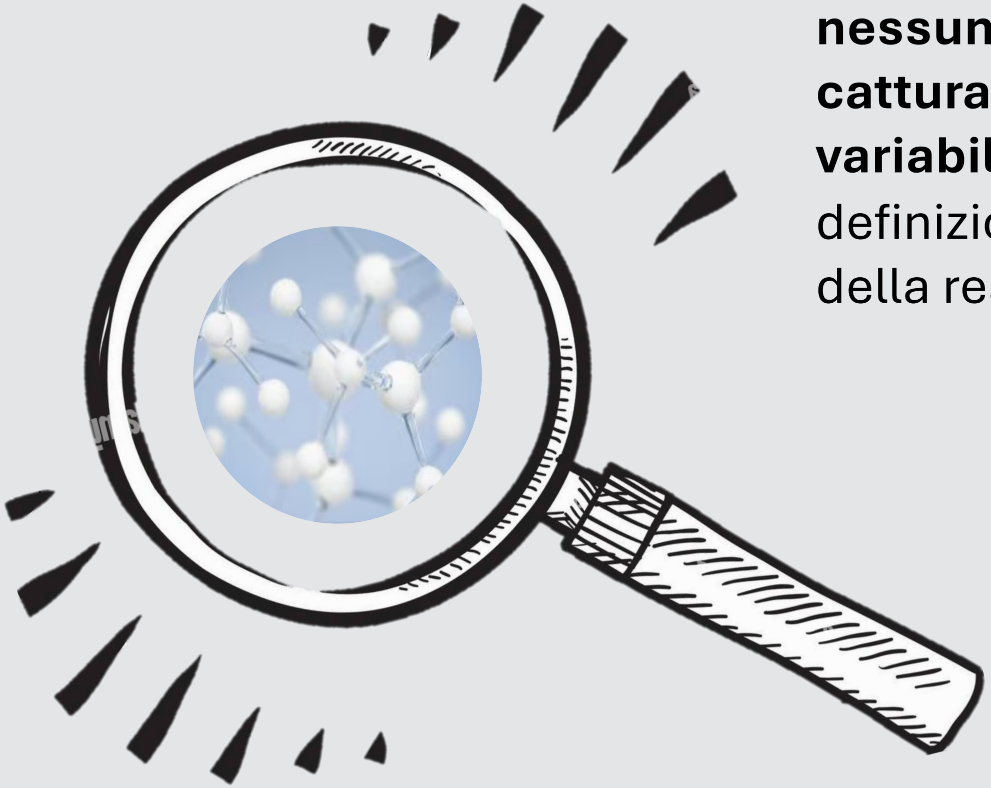
La chimica è il racconto dell'invisibile, narrato attraverso i modelli



Uno dei compiti più delicati nell'insegnare chimica è far comprendere mondi composti da oggetti troppo piccoli e troppo numerosi per essere immaginati.

I modelli sono ponti indispensabili tra realtà e mente.

Come diceva George Box: *'All models are wrong, but some are useful'* — ed è nostro compito aiutare gli studenti a capire in che senso sono utili.



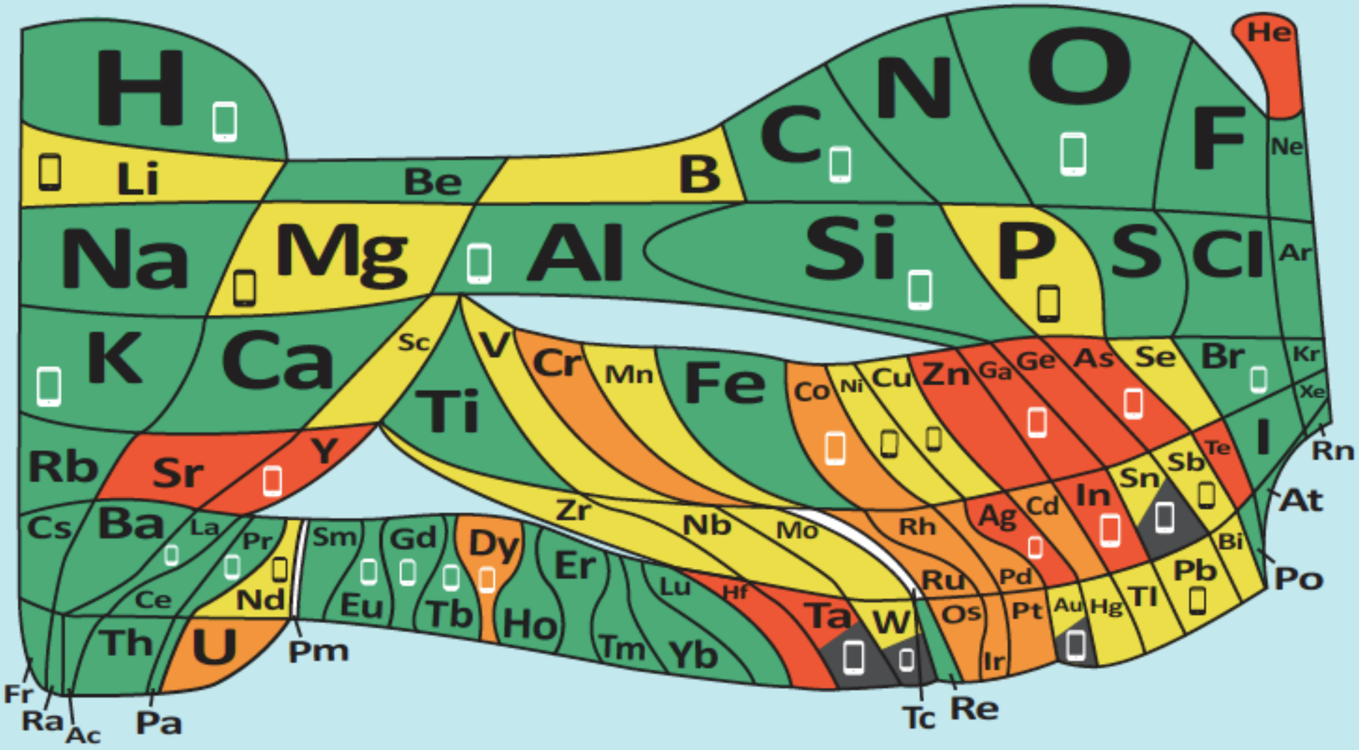
nessun modello matematico o statistico può catturare completamente la complessità e la variabilità del mondo reale. Un modello è, per definizione, una rappresentazione semplificata della realtà, e quindi un'approssimazione

United Nations
Educational, Scientific and
Cultural Organization

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

The 90 natural elements that make up everything

How much is there? Is that enough?


H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Xe
Ti
Rb
Sr
Y
I
Rn
Te
Sb
Sn
In
Cd
Ag
Rh
Mo
Nb
Zr
At
Cs
Ba
La
Pr
Sm
Gd
Dy
Er
Bi
Po
Pb
Pd
Ru
Ce
Nd
Eu
Tb
Ho
Lu
Hf
Ta
W
Os
Pt
Au
Hg
Tl
Th
U
Pm
Tm
Yb
Ir
Fr
Ra
Ac
Pa
Tc
Re

🟥 **Serious threat in the next 100 years**

🟧 **Rising threat from increased use**

🟨 **Limited availability, future risk to supply**

🟩 **Plentiful Supply**

⬜ **Synthetic**

⬛ **From conflict minerals**

📱 **Elements used in a smart phone**

Read more and play the video game **http://bit.ly/euchems-pt**

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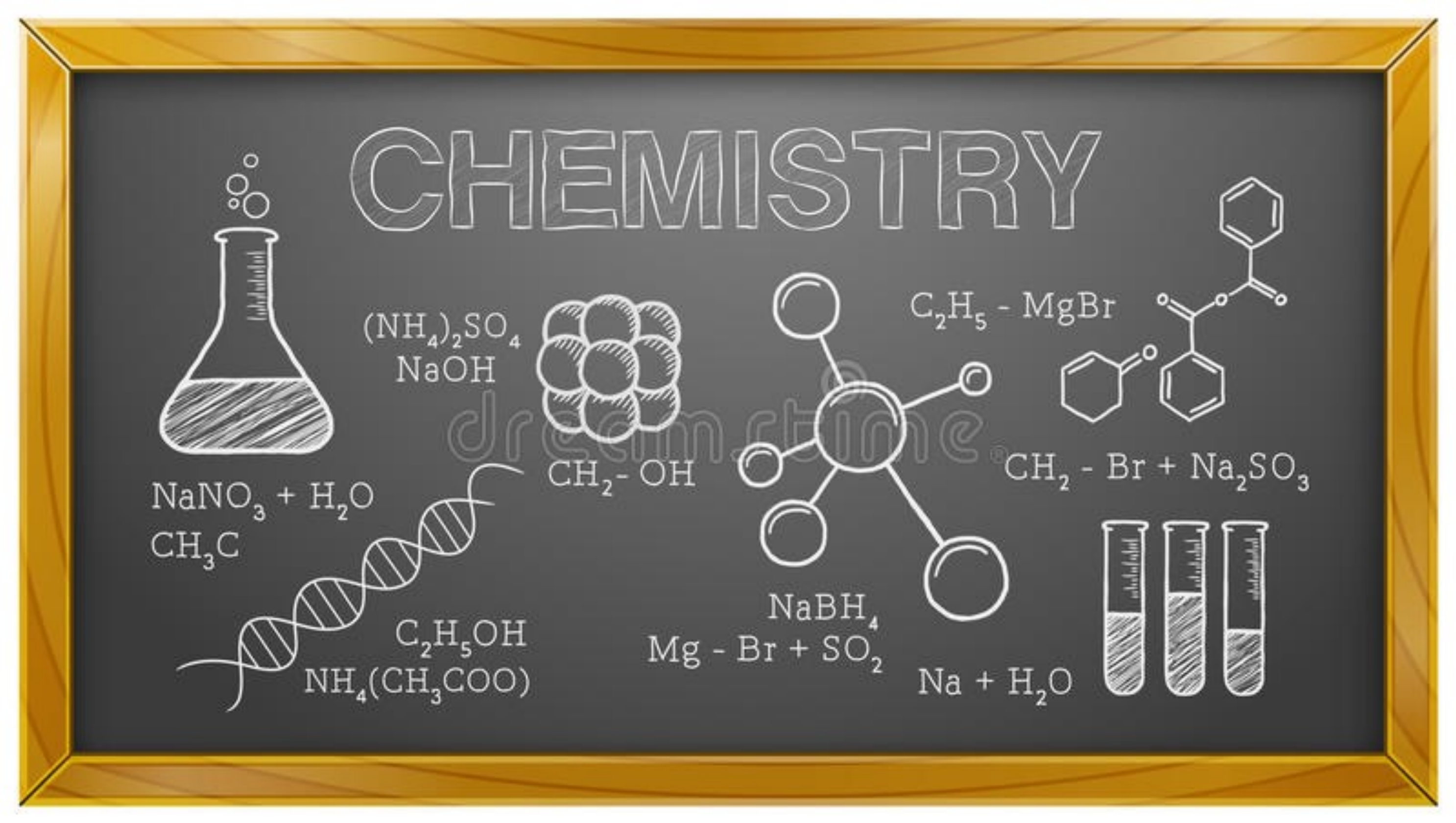
EuChemS
European Chemical Society

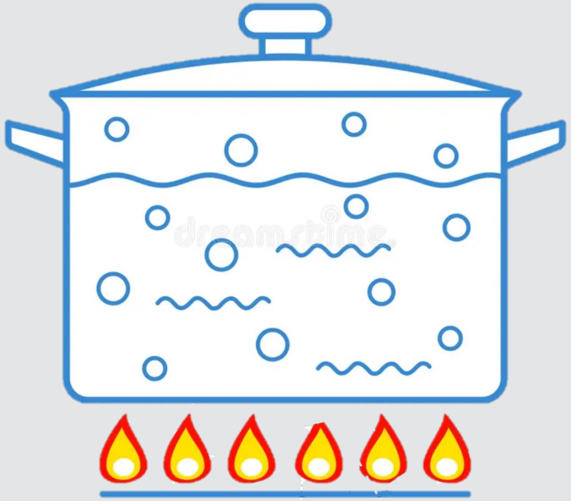
Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18'

[redacted]


CHEMISTRY
$(NH_4)_2SO_4$
NaOH
C_2H_5 - MgBr
$NaNO_3 + H_2O$
CH_3C
CH_2- OH
CH_2 - Br + Na_2SO_3
$NaBH_4$
Mg - Br + SO_2
C_2H_5OH
$NH_4(CH_3COO)$
Na + H_2O

$U = U(T,V)$

- Differenziale esatto



$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

A quale domanda risponde la Termodinamica Classica?

Qual è la direzione dei processi spontanei

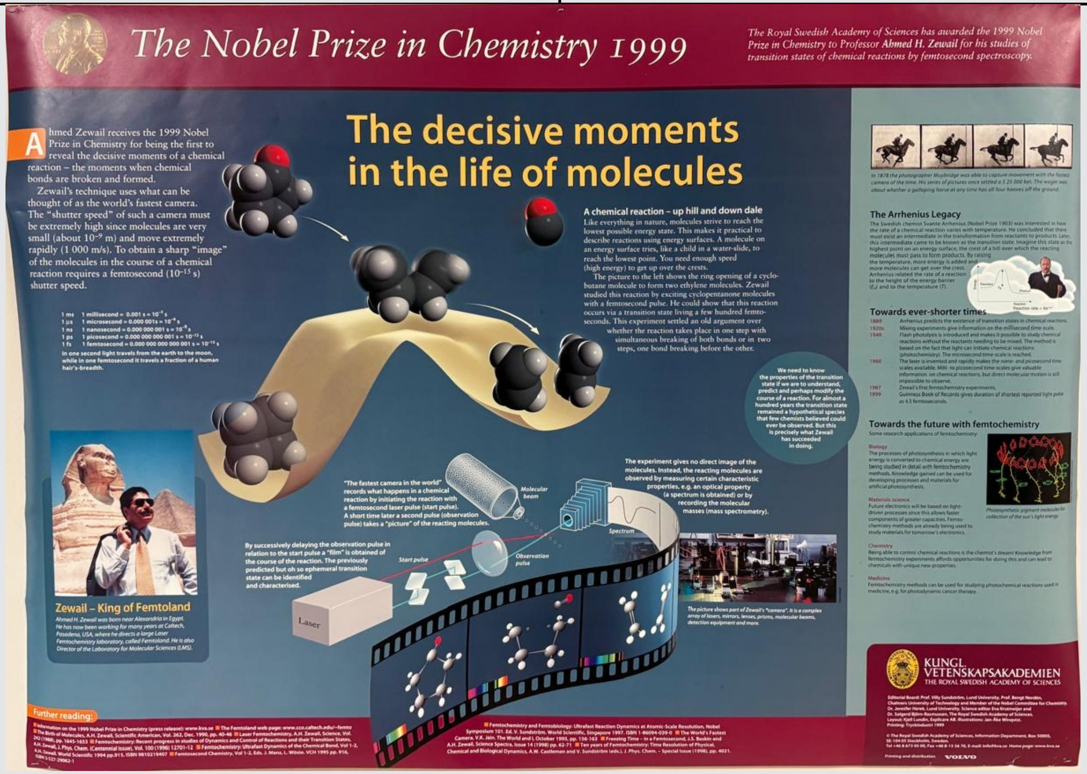
- La spontaneità è la capacità di un processo di avvenire senza interventi esterni
- Accade "naturalmente"

- **Termodinamica: un processo è spontaneo se avviene senza che venga eseguito del lavoro sul sistema.**

Anno	Scienziato - Scoperta	Tecnologie disponibili all’epoca
1824	Carnot- Ciclo di Carnot, inizio termodinamica	Macchine a vapore, caldaie, termometri a mercurio, manometri
1850	Clausius - I principio e entropia	Calorimetri, turbine a vapore, strumenti di misura termodinamici
1850s	Kelvin – II principio	Scale termometriche precise, frigoriferi sperimentali, pompe di calore
1864	Guldberg & Waage – Legge di azione di massa	Bilance di precisione, burette, titolazioni chimiche
1870s	Gibbs – Energia libera ΔG	Tavole termodinamiche, analisi chimiche sistematiche
1889	Arrhenius – Equazione di Arrhenius	Cronometri meccanici, termometri precisi, laboratori controllati

1900	Planck – Ipotesi dei quanti	Lampade a incandescenza, spettroscopia ottica classica
1905	Einstein – Effetto fotoelettrico	Fotocellule rudimentali, tubi catodici, elettroscopi
1906	Nernst – III principio	Criogenia iniziale (azoto e ossigeno liquidi), calorimetria a bassa T
1913	Bohr – Modello atomico quantizzato	Spettroscopi a prisma, reticoli di diffrazione, tubi a scarica
1913	Trautz & Lewis – Teoria delle collisioni	Teoria cinetica dei gas, esperimenti in fase gassosa
1924	de Broglie – Dualità onda-particella	Tubi a vuoto, analogie con ottica classica
1926	Schrödinger – Equazione d’onda	Calcolo matematico avanzato, dati spettroscopici
1927	Heisenberg – Principio di indeterminazione	Esperimenti su elettroni e fotoni, spettroscopia avanzata

1935	Eyring – Teoria dello stato di transizione	Curve di energia potenziale, cinetica chimica avanzata
1999	Zewail – Femtrochimica (Nobel)	Laser a femtosecondi, rilevatori elettronici ultraveloci, computer digitali



The Nobel Prize in Chemistry 1999

*The Royal Swedish Academy of Sciences has awarded the 1999 Nobel Prize in Chemistry to Professor **Ahmed H. Zewail** for his studies of transition states of chemical reactions by femtosecond spectroscopy.*

The decisive moments in the life of molecules

Ahmed Zewail receives the 1999 Nobel Prize in Chemistry for being the first to reveal the decisive moments of a chemical reaction – the moments when chemical bonds are broken and formed.

Zewail's technique uses what can be thought of as the world's fastest camera. The "shutter speed" of such a camera must be extremely high since molecules are very small (about 10^{-9} m) and move extremely rapidly (1 000 m/s). To obtain a sharp "image" of the molecules in the course of a chemical reaction requires a femtosecond (10^{-15} s) shutter speed.

1 ms 1 millisecond = 0.001 s = 10^{-3} s
1 µs 1 microsecond = 0.000 001s = 10^{-6} s
1 ns 1 nanosecond = 0.000 000 001 s = 10^{-9} s
1 ps 1 picosecond = 0.000 000 000 001 s = 10^{-12} s
1 fs 1 femtosecond = 0.000 000 000 000 001 s = 10^{-15} s

In one second light travels from the earth to the moon, while in one femtosecond it travels a fraction of a human hair's-breadth.

A chemical reaction – up hill and down dale
Like everything in nature, molecules strive to reach the lowest possible energy state. This makes it practical to describe reactions using energy surfaces. A molecule on an energy surface tries, like a child in a water-slide, to reach the lowest point. You need enough speed (high energy) to get up over the crests.

The picture to the left shows the ring opening of a cyclobutane molecule to form two ethylene molecules. Zewail studied this reaction by exciting cyclopentanone molecules with a femtosecond pulse. He could show that this reaction occurs via a transition state living a few hundred femtoseconds. This experiment settled an old argument over whether the reaction takes place in one step with simultaneous breaking of both bonds or in two steps, one bond breaking before the other.

We need to know the properties of the transition state if we are to understand, predict and perhaps modify the course of a reaction. For almost a hundred years the transition state remained a hypothetical species that few chemists believed could ever be observed. But this is precisely what Zewail has succeeded in doing.

"The fastest camera in the world" records what happens in a chemical reaction by initiating the reaction with a femtosecond laser pulse (start pulse). A short time later a second pulse (observation pulse) takes a "picture" of the reacting molecules.

By successively delaying the observation pulse in relation to the start pulse a "film" is obtained of the course of the reaction. The previously predicted but oh so ephemeral transition state can be identified and characterised.

The experiment gives no direct image of the molecules. Instead, the reacting molecules are observed by measuring certain characteristic properties, e.g. an optical property (a spectrum is obtained) or by recording the molecular masses (mass spectrometry).

The picture shows part of Zewail's "camera". It is a complex array of lasers, mirrors, lenses, prisms, molecular beams, detection equipment and more.

Zewail – King of Femtoland
Ahmed H. Zewail was born near Alexandria in Egypt. He has now been working for many years at Caltech, Pasadena, USA, where he directs a large Laser Femtochemistry laboratory, called Femtoland. He is also Director of the Laboratory for Molecular Sciences (LMS).

In 1878 the photographer Muybridge was able to capture movement with the fastest camera of the time. His series of pictures once settled a $ 25 000 bet. The wager was about whether a galloping horse at any time has all four hooves off the ground.

The Arrhenius Legacy
The Swedish chemist Svante Arrhenius (Nobel Prize 1903) was interested in how the rate of a chemical reaction varies with temperature. He concluded that there must exist an intermediate in the transformation from reactants to products. Later, this intermediate came to be known as the transition state. Imagine this state as the highest point on an energy surface, the crest of a hill over which the reacting molecules must pass to form products. By raising the temperature, more energy is added and more molecules can get over the crest. Arrhenius related the rate of a reaction to the height of the energy barrier (E_a) and to the temperature (T).

Towards ever-shorter times

1889	Arrhenius predicts the existence of transition states in chemical reactions.
1920s	Mixing experiments give information on the millisecond time-scale.
1949	Flash photolysis is introduced and makes it possible to study chemical reactions without the reactants needing to be mixed. The method is based on the fact that light can initiate chemical reactions (photochemistry). The microsecond time-scale is reached.
1960	The laser is invented and rapidly makes the *nano-* and *picosecond* time scales available. Milli- to picosecond time-scales give valuable information on chemical reactions, but direct molecular motion is still impossible to observe.
1987	Zewail's first femtochemistry experiments.
1999	Guinness Book of Records gives duration of shortest reported light pulse as 4.5 femtoseconds.

Towards the future with femtochemistry
Some research applications of femtochemistry.

Biology
The processes of photosynthesis in which light energy is converted to chemical energy are being studied in detail with femtochemistry methods. Knowledge gained can be used for developing processes and materials for artificial photosynthesis.

Photosynthetic pigment molecules for collection of the sun's light energy

Materials science
Future electronics will be based on light-driven processes since this allows faster components of greater capacities. Femtochemistry methods are already being used to study materials for tomorrow's electronics.

Chemistry
Being able to control chemical reactions is the chemist's dream! Knowledge from femtochemistry experiments affords opportunities for doing this and can lead to chemicals with unique new properties.

Medicine
Femtochemistry methods can be used for studying photochemical reactions used in medicine, e.g. for photodynamic cancer therapy.

Further reading:
Information on the 1999 Nobel Prize in Chemistry (press release): www.kva.se ■ The Femtoland web page: www.cco.caltech.edu/~femto ■ The Birth of Molecules, A.H. Zewail, Scientific American, Vol. 262, Dec. 1990, pp. 40-46 ■ Laser Femtochemistry, A.H. Zewail, Science, Vol. 242 (1988), pp. 1645-1653 ■ Femtochemistry: Recent progress in studies of Dynamics and Control of Reactions and their Transition States, A.H. Zewail, J. Phys. Chem. (Centennial Issue), Vol. 100 (1996) 12701-12 ■ Femtochemistry: Ultrafast Dynamics of the Chemical Bond, Vol 1-2, A.H. Zewail, World Scientific 1994 pp.915, ISBN 9810219407 ■ Femtosecond Chemistry, Vol 1-2, Eds. J. Manz, L. Wöste. VCH 1995 pp. 916, ISBN 3-527-29062-1 ■ Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution, Nobel Symposium 101. Ed. V. Sundström. World Scientific, Singapore 1997. ISBN 1-86094-039-0 ■ The World's Fastest Camera, V.K. Jain. The World and I, October 1995, pp. 156-163 ■ Freezing Time – in a Femtosecond, J.S. Baskin and A.H. Zewail, Science Spectra, Issue 14 (1998) pp. 62-71 ■ Ten years of Femtochemistry: Time Resolution of Physical, Chemical and Biological Dynamics, A.W. Castleman and V. Sundström (eds.), J. Phys. Chem. – Special Issue (1998), pp. 4021.

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

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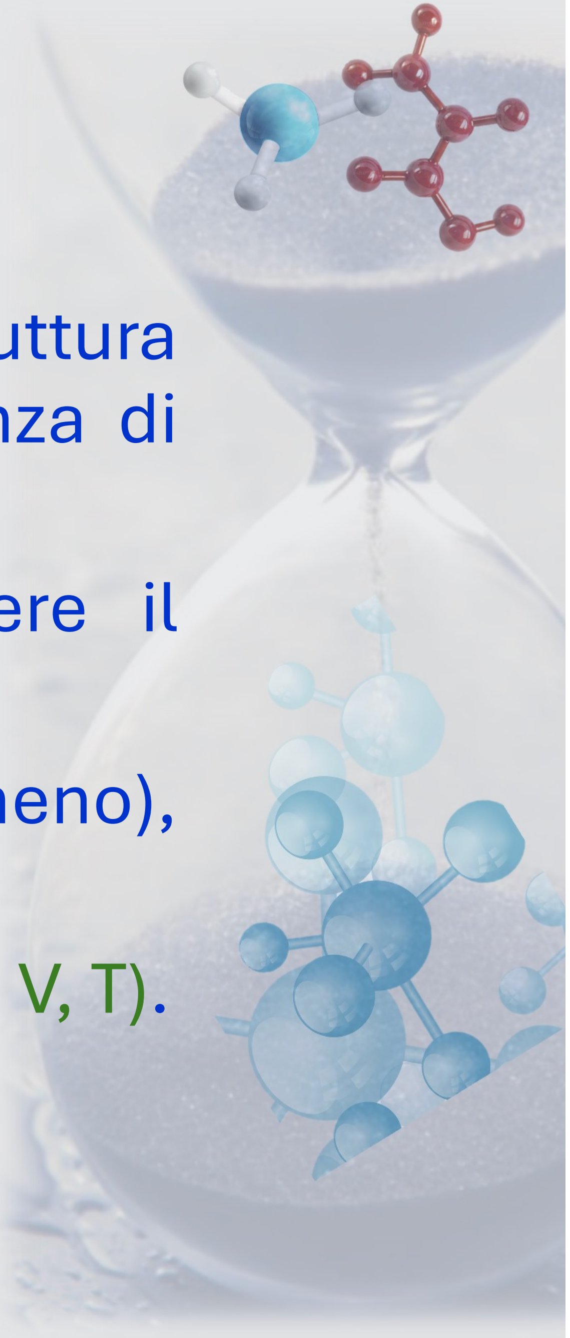
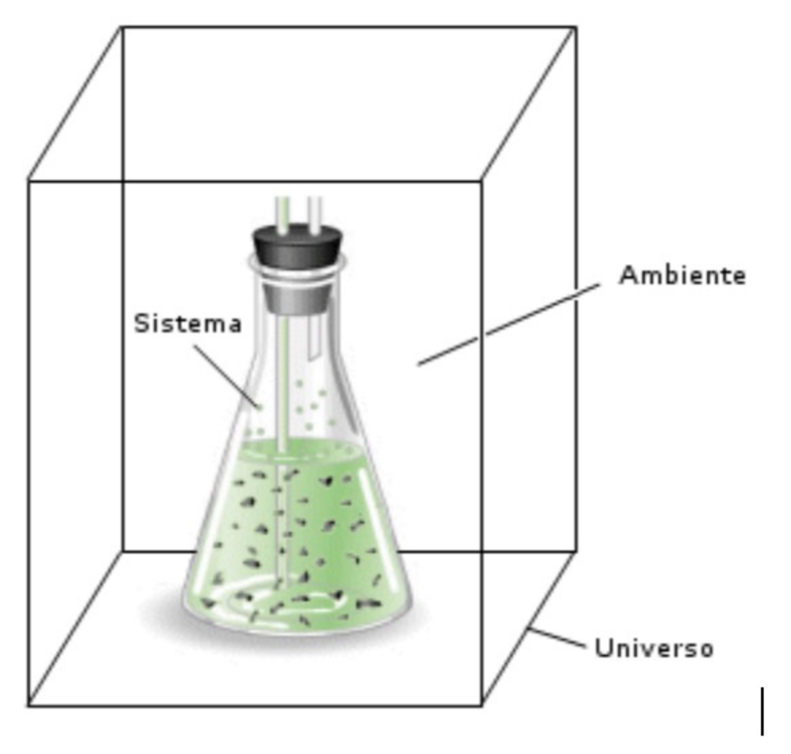
Grandezze Macroscopiche



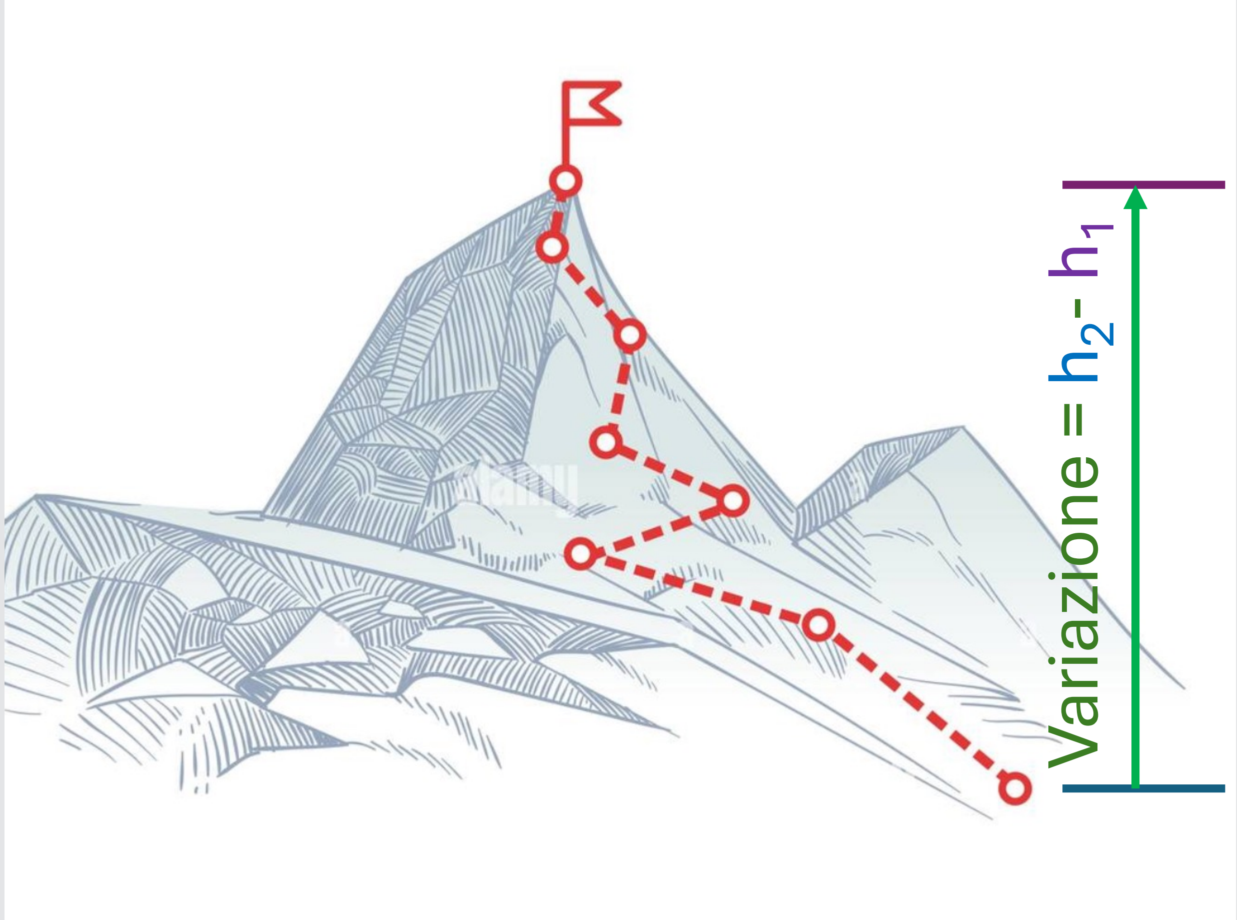
- NON implicano ipotesi particolari sulla struttura della materia (non richiedono la conoscenza di atomi e molecole!);
- Servono “poche” grandezze per descrivere il sistema;
- Le coordinate macroscopiche sono (più o meno), suggerite dai nostri sensi;
- Possono essere misurate direttamente (n, p, V, T).

Sistema, Ambiente e Universo

- Nello studio di un fenomeno, si cerca di isolare la ‘zona di spazio’ dove avviene il fenomeno da quello che la circonda.


Ambiente
Sistema
Universo

Funzioni di stato

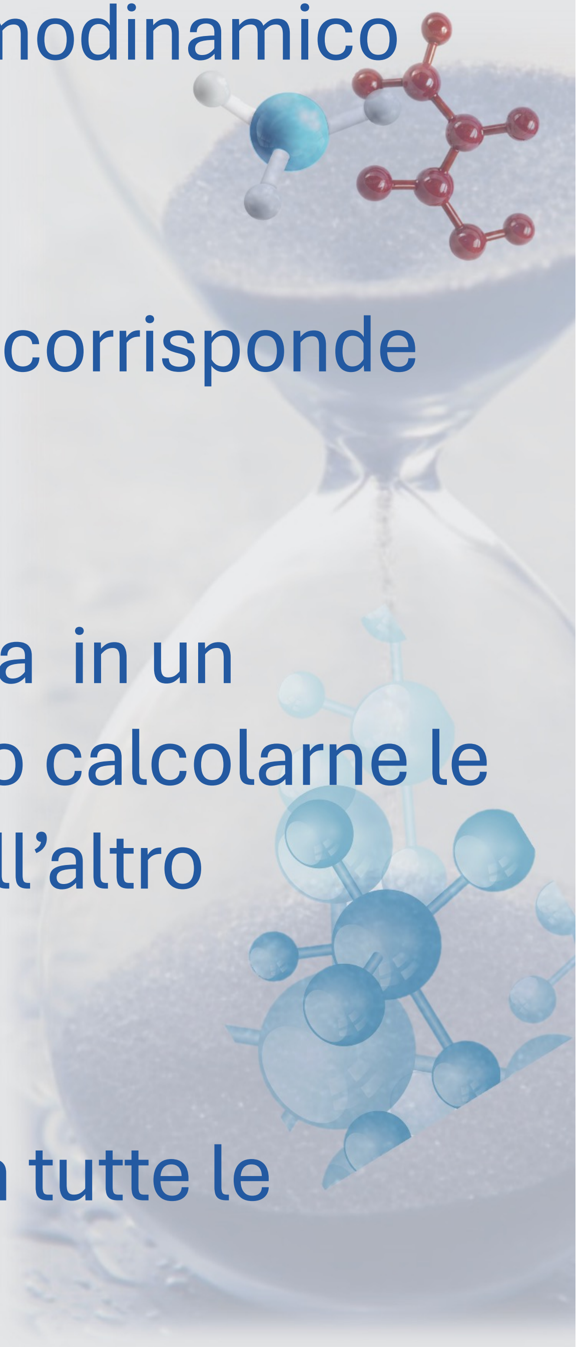


Stato finale h_2

Variazione = $h_2 - h_1$

Stato iniziale h_1

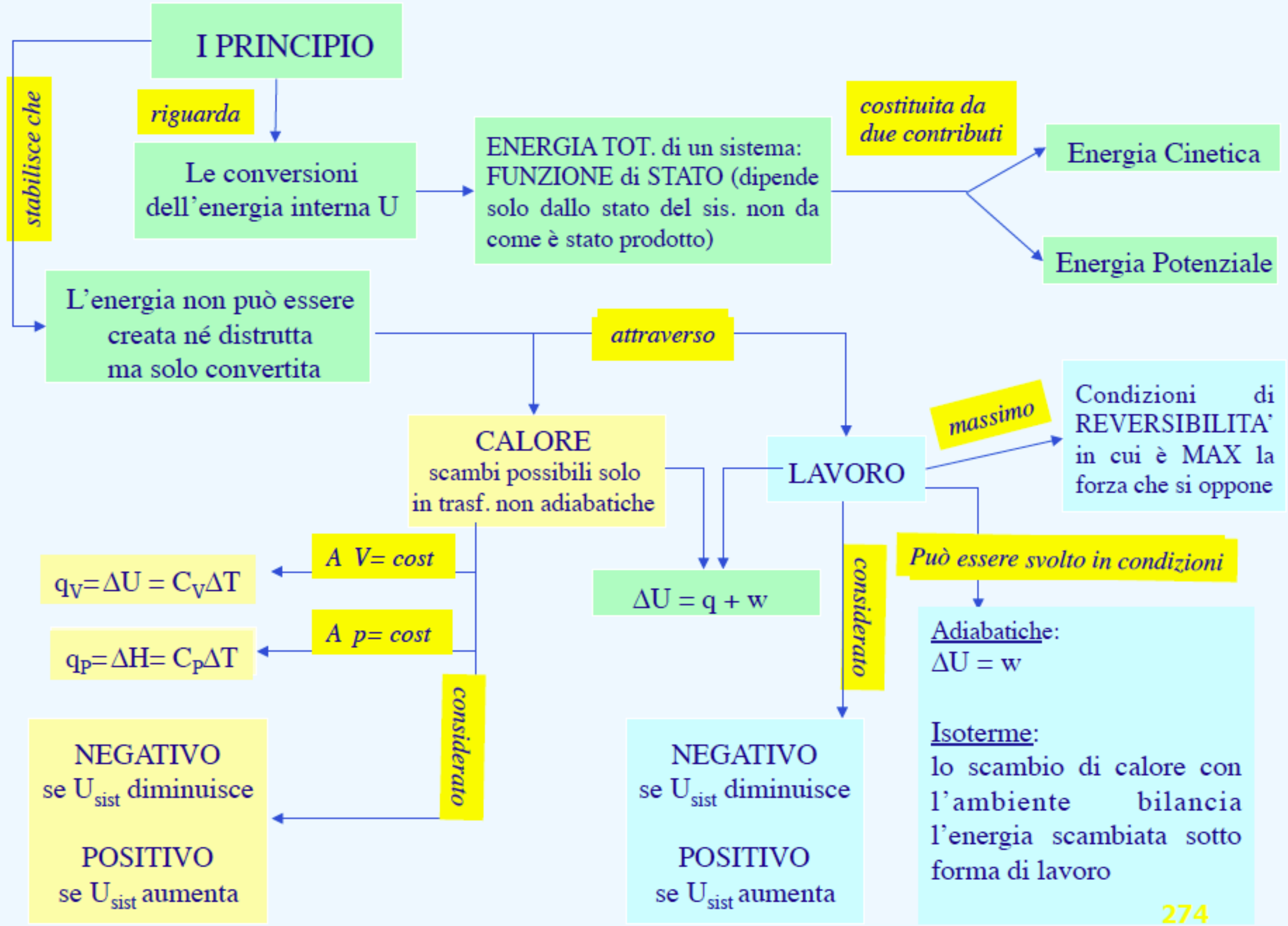
- I valori di n, p, V, T definiscono lo stato termodinamico del sistema
- Ad ogni stato termodinamico del sistema corrisponde un valore di energia (cinetica +potenziale)
- Non posso conoscere l'energia del sistema in un particolare stato termodinamico ma posso calcolarne le variazioni quando si muove da uno stato all'altro indipendentemente dal percorso
- Non esiste uno zero dell'energia comune a tutte le sostanze



Energie Termodinamiche

Energia Interna (U, sufficiente per descrivere processi a V costante)

Entalpia (H, necessaria per descrivere i processi a p costante)



I PRINCIPIO

stabilisce che

riguarda

Le conversioni dell'energia interna U

ENERGIA TOT. di un sistema: FUNZIONE di STATO (dipende solo dallo stato del sis. non da come è stato prodotto)

costituita da due contributi

Energia Cinetica

Energia Potenziale

L'energia non può essere creata né distrutta ma solo convertita

attraverso

CALORE
scambi possibili solo in trasf. non adiabatiche

LAVORO

massimo

Condizioni di REVERSIBILITA' in cui è MAX la forza che si oppone

Può essere svolto in condizioni

A V= cost

$q_V = \Delta U = C_V \Delta T$

A p= cost

$q_P = \Delta H = C_P \Delta T$

$\Delta U = q + w$

considerato

NEGATIVO
se U_{sist} diminuisce

POSITIVO
se U_{sist} aumenta

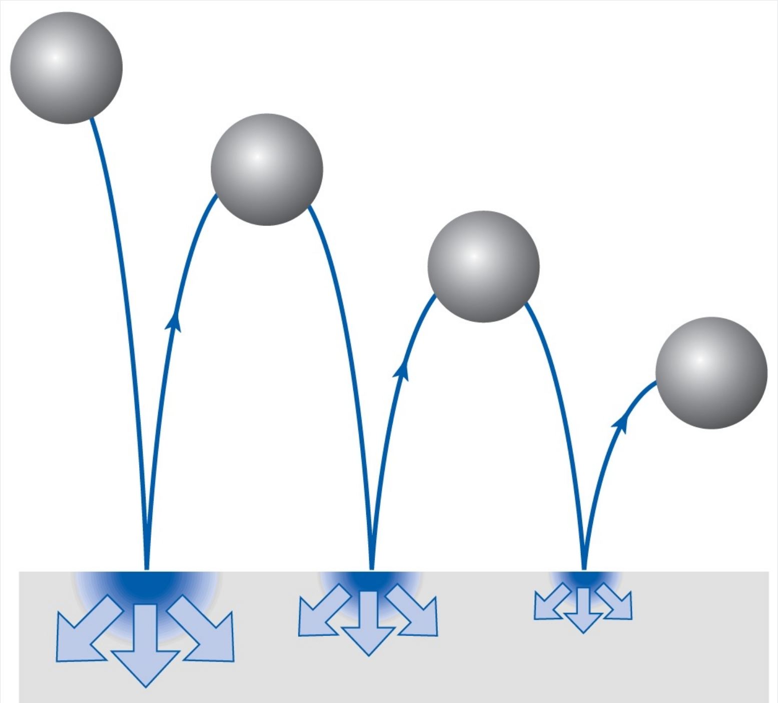
considerato

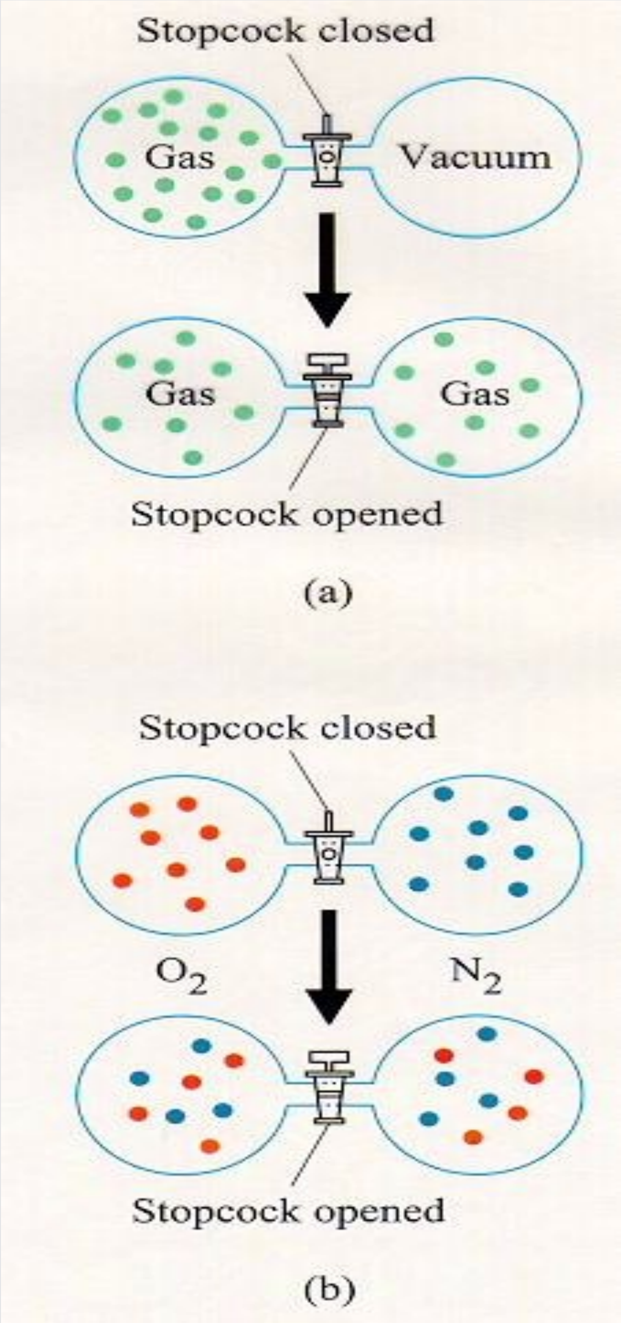
NEGATIVO
se U_{sist} diminuisce

POSITIVO
se U_{sist} aumenta

Adiabatiche:
$\Delta U = w$

Isoterme:
lo scambio di calore con l'ambiente bilancia l'energia scambiata sotto forma di lavoro




Stopcock closed
Gas
Vacuum
Gas
Gas
Stopcock opened
(a)
Stopcock closed
O_2
N_2
Stopcock opened
(b)

Entropia - Identikit

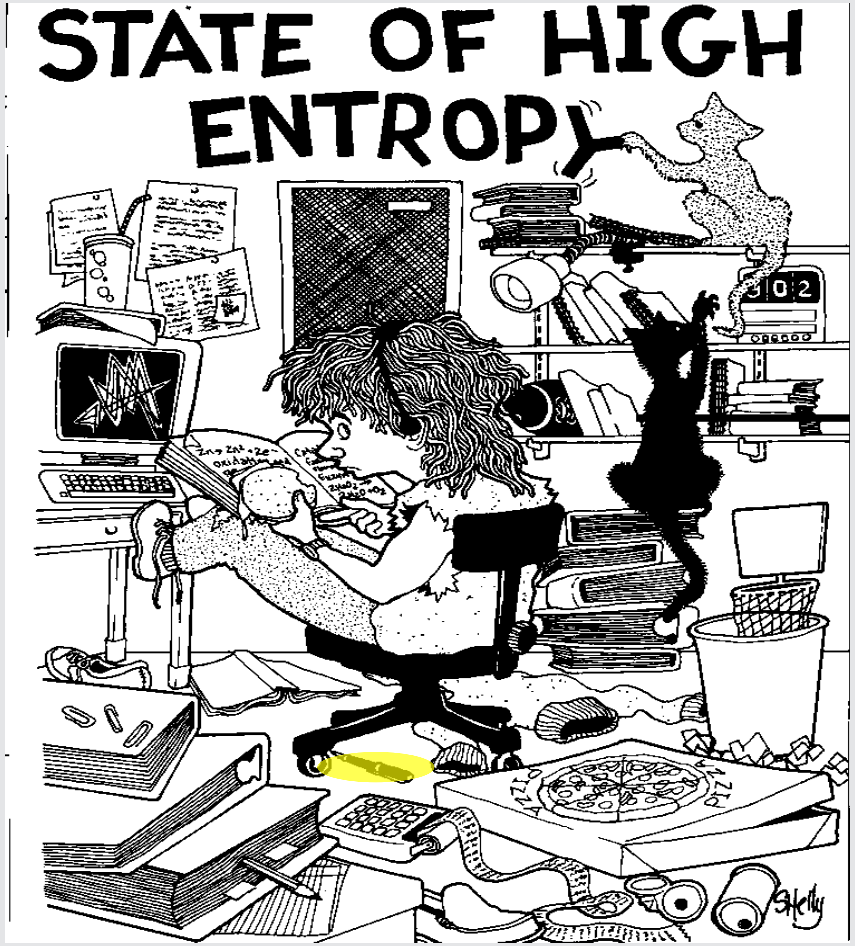
- Deve essere una funzione di stato
- Deve aumentare in un processo spontaneo
- Deve avere a che fare con la “dispersione caotica” della materia e dell’energia
- Deve dipendere dalla temperatura

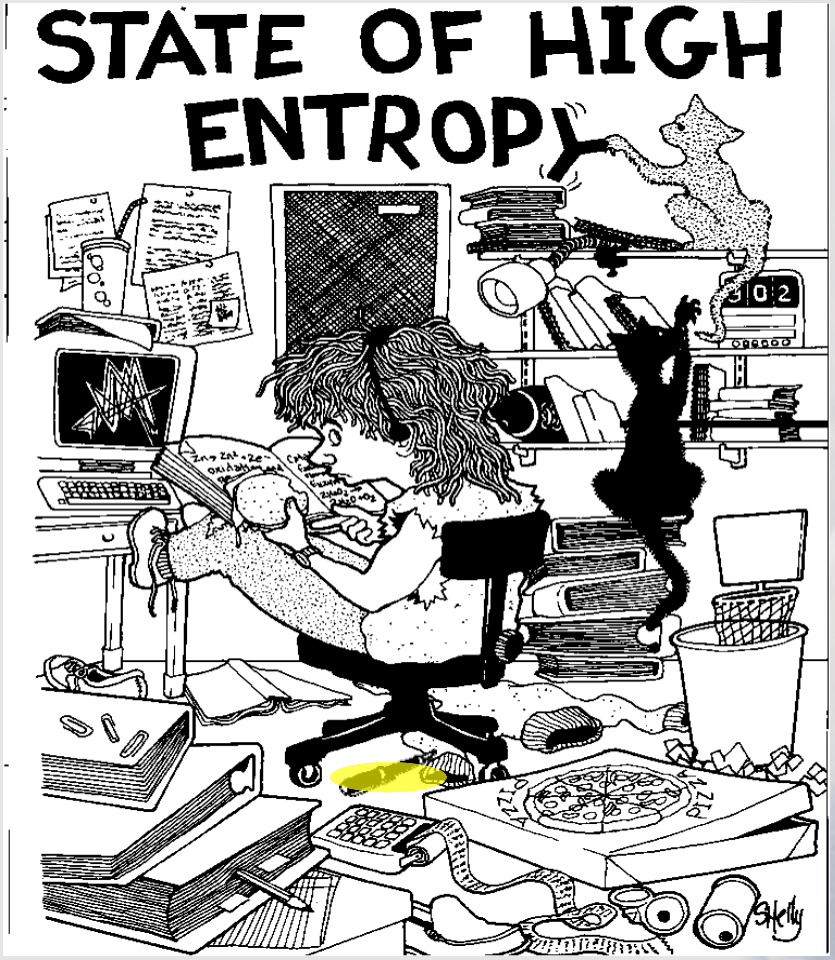
DEFINIZIONE TERMODINAMICA DELL’ENTROPIA

$$\boxed{dS = dq_{rev}/T}$$

PRIMA

DOPO

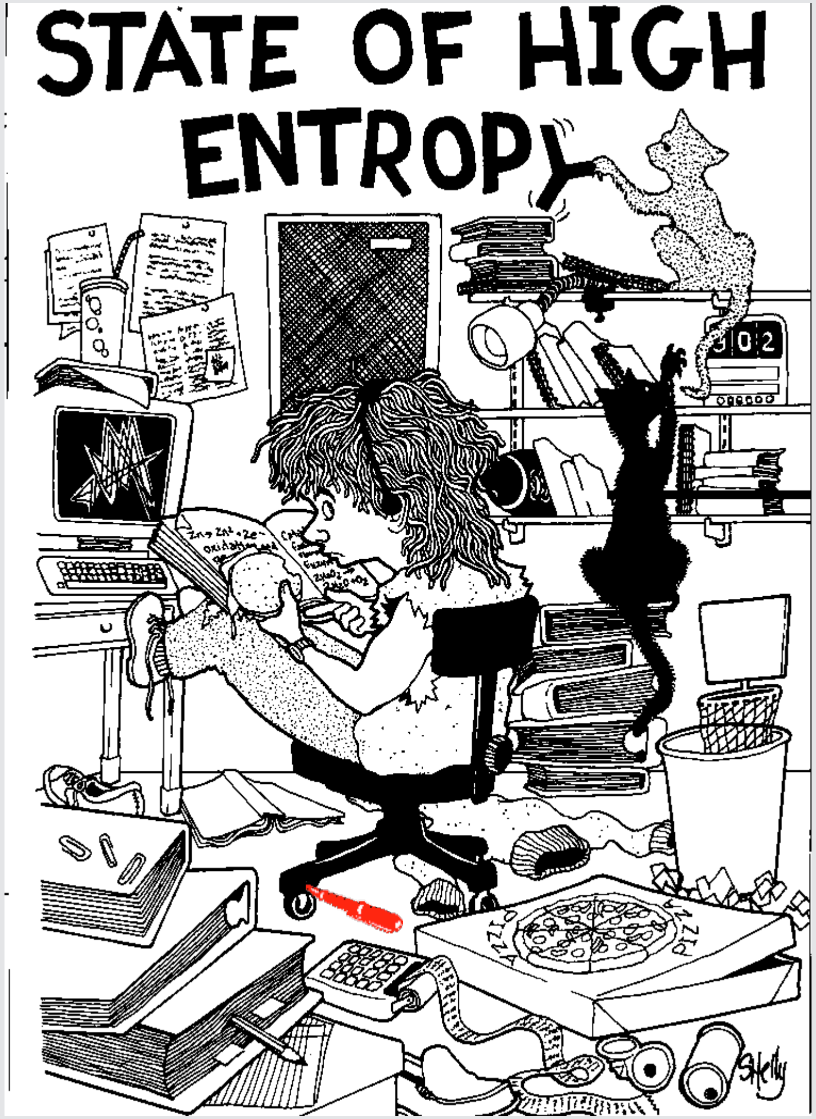

STATE OF HIGH ENTROPY
PIZZA
Shelly


STATE OF HIGH ENTROPY
PIZZA
Shelly

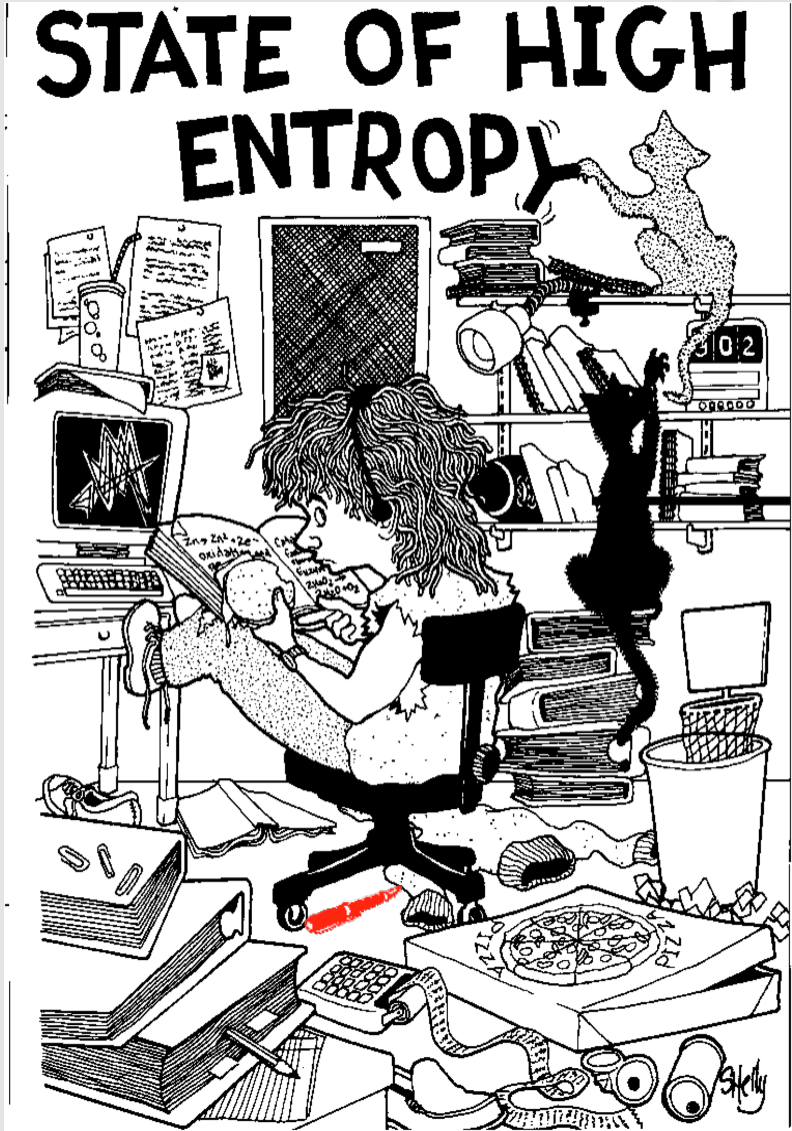
PRIMA

DOPO

PRIMA


STATE OF HIGH ENTROPY
302
PIZZA
Shelly

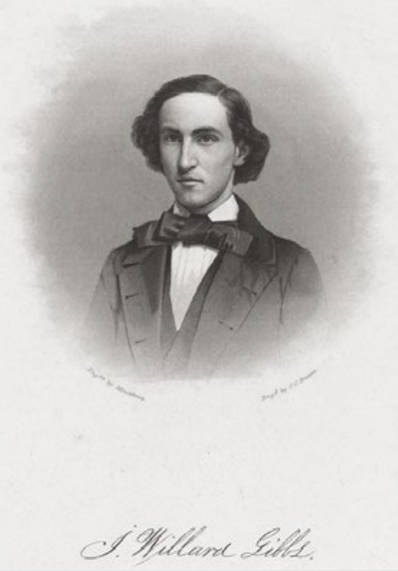
DOPO


STATE OF HIGH ENTROPY
302
PIZZA
Shelly

007 La Borgesiana Biblioteca di Babele! © Paolo Moisello

quale libreria è possibile disordinare di più?

Criteri di Spontaneità

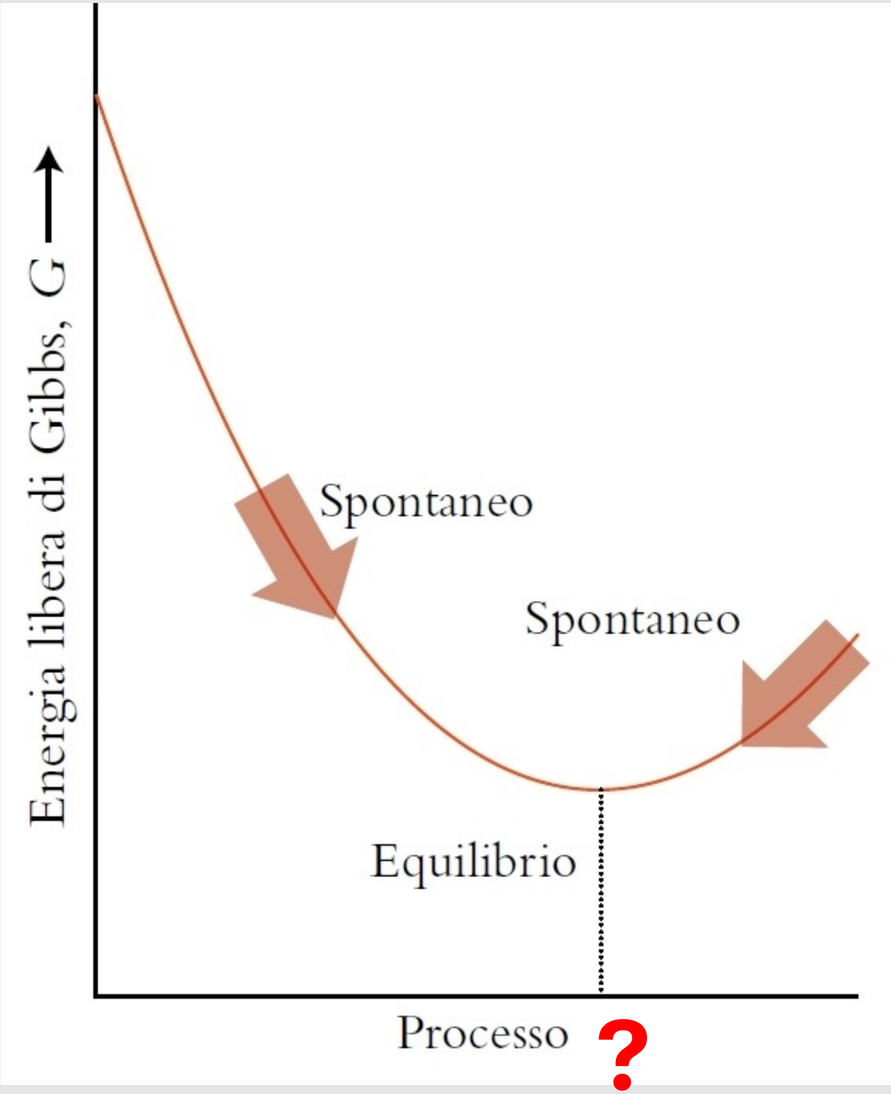

J. Willard Gibbs

$$\Delta S_{amb} + \Delta S_{sis} > 0$$

$$\Delta G_{sis} < 0$$ a p e T costanti

$$\Delta G_{sis}^{\circ} = \Delta H_{sis}^{\circ} - T\Delta S_{sis}^{\circ}$$

-	+	SEMPRE
-	-	BASSE T
+	+	ALTE T
+	-	MAI


Energia libera di Gibbs, G →
Spontaneo
Spontaneo
Equilibrio
Processo
?

*Gibbs
$\Delta G = \Delta G^\circ + RT \ln Q$
*Nernst
Chimica del Suicidio
$\Delta G = \Delta G^\circ + RT \ln Q$
$\frac{\Delta G}{nF} = \frac{\Delta G^\circ}{nF} - \frac{RT}{nF} \ln Q$

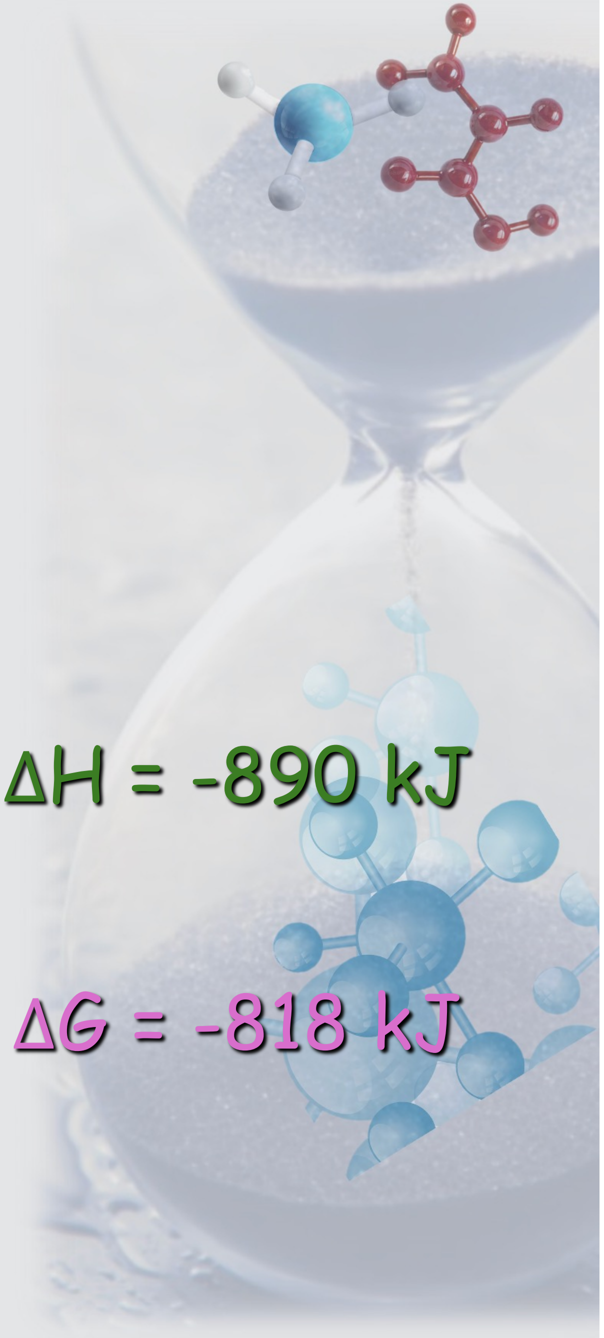
$CH_4 + O_2 \rightarrow CO_2 + H_2O$

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ $\Delta H = -890\ kJ$

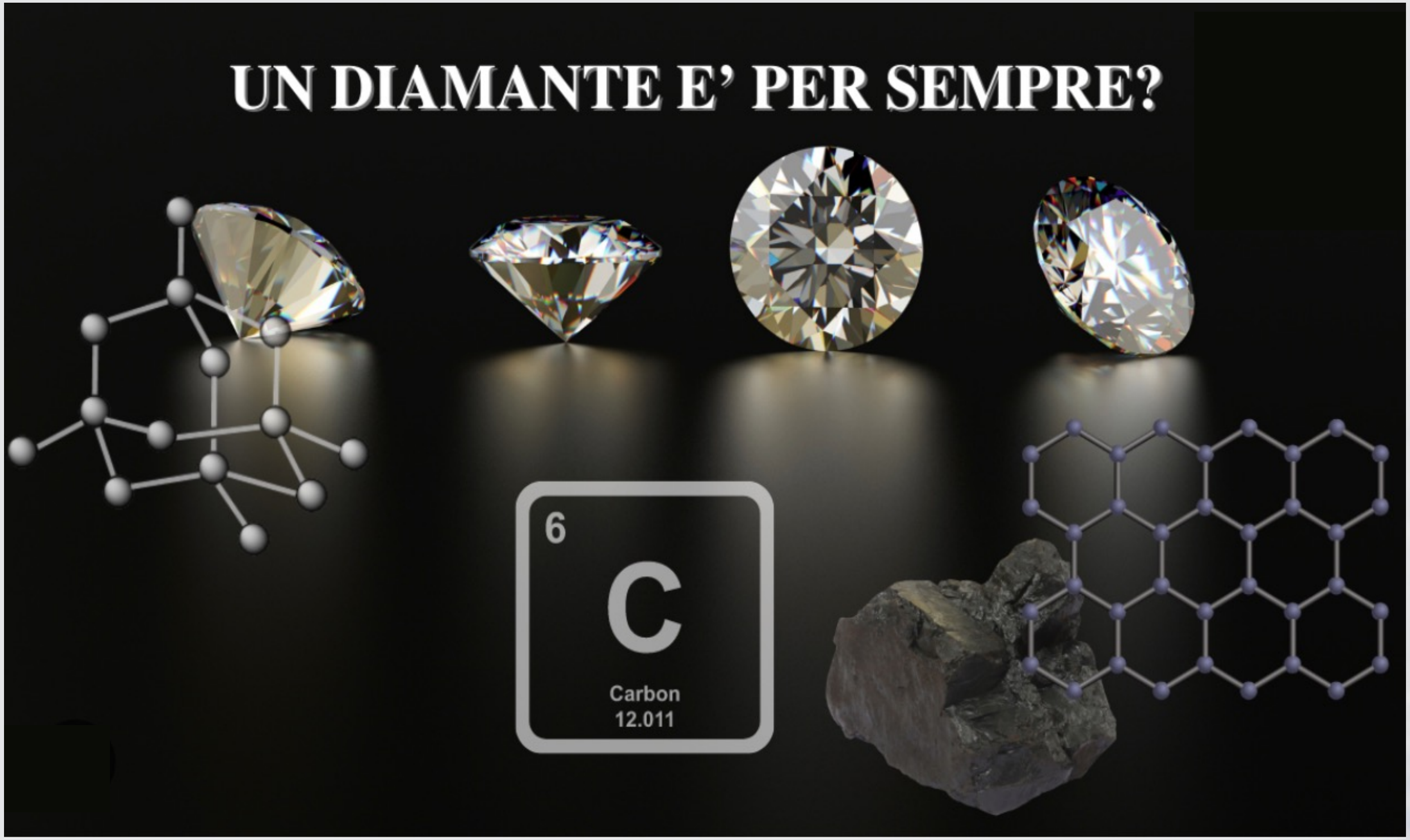
$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ $\Delta G = -818\ kJ$

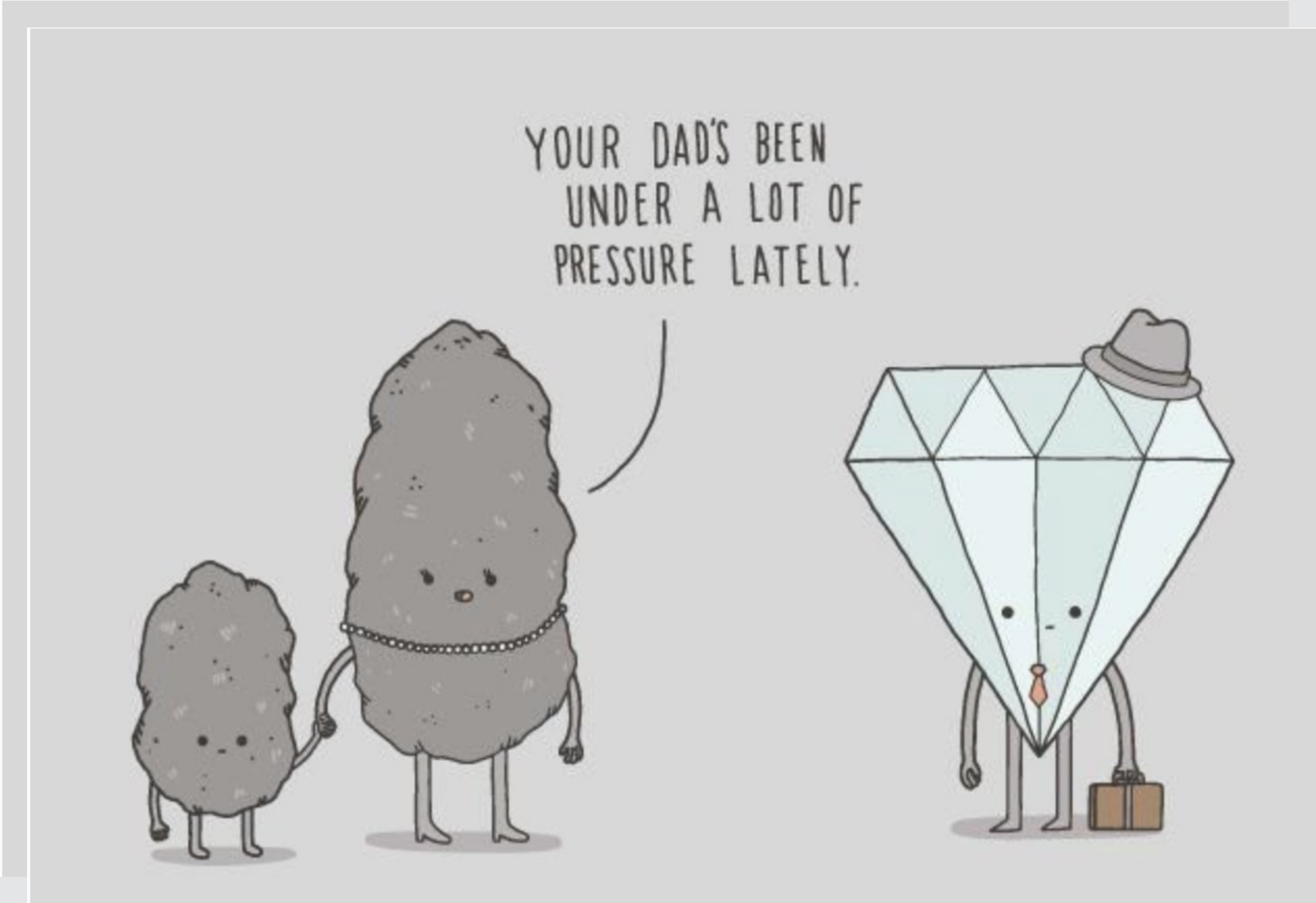


$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

Grandezza	Valore	Unità	Osservazioni
$\Delta H°$	-890.3	kJ/mol	Reazione molto esotermica (libera calore).
$\Delta G°$	-817.8	kJ/mol	Energia libera disponibile per lavoro utile.
$\Delta S°$	-243	J/(mol·K)	Diminuzione di entropia: da 3 moli di gas → 1 mole di gas + 2moli di liquido.

UN DIAMANTE E' PER SEMPRE?

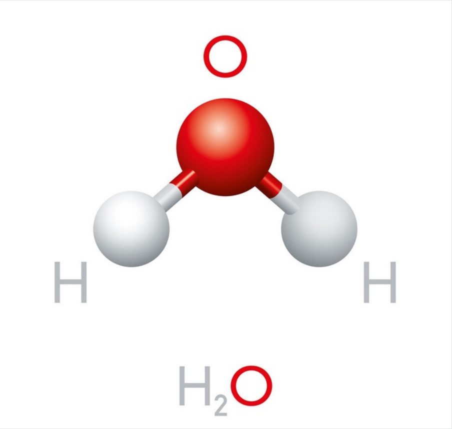

6
C
Carbon
12.011

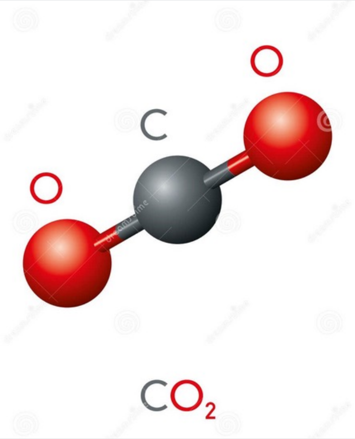

YOUR DAD'S BEEN UNDER A LOT OF PRESSURE LATELY.

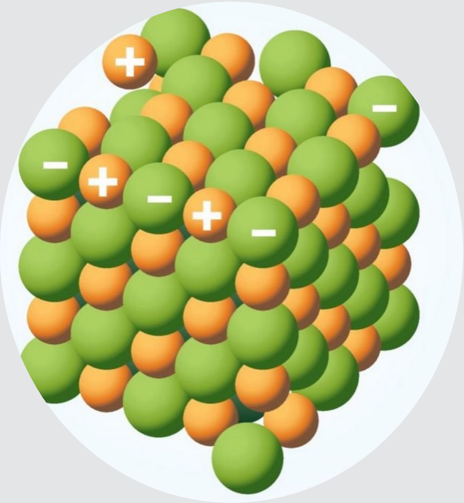
Grandezze Microscopiche

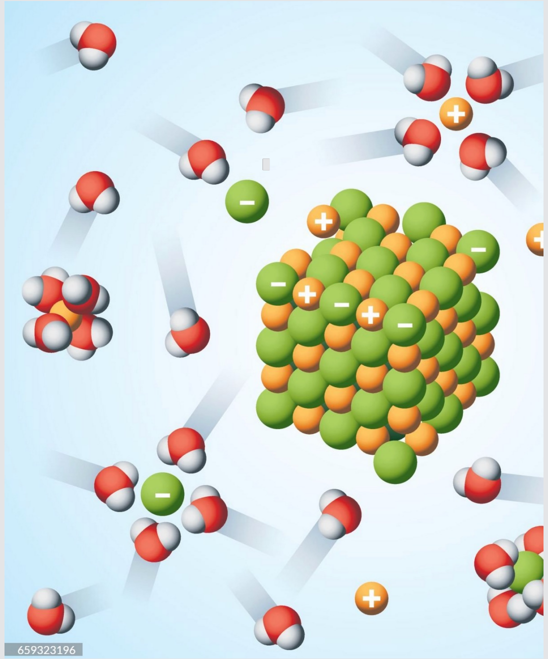
- Si DEVE ipotizzare l'esistenza degli atomi e molecole
- Le coordinate in gioco sono tantissime (*N*)
- Le varie grandezze NON sono accessibili nell'esperienza quotidiana.
- Le grandezze microscopiche NON si possono misurare direttamente

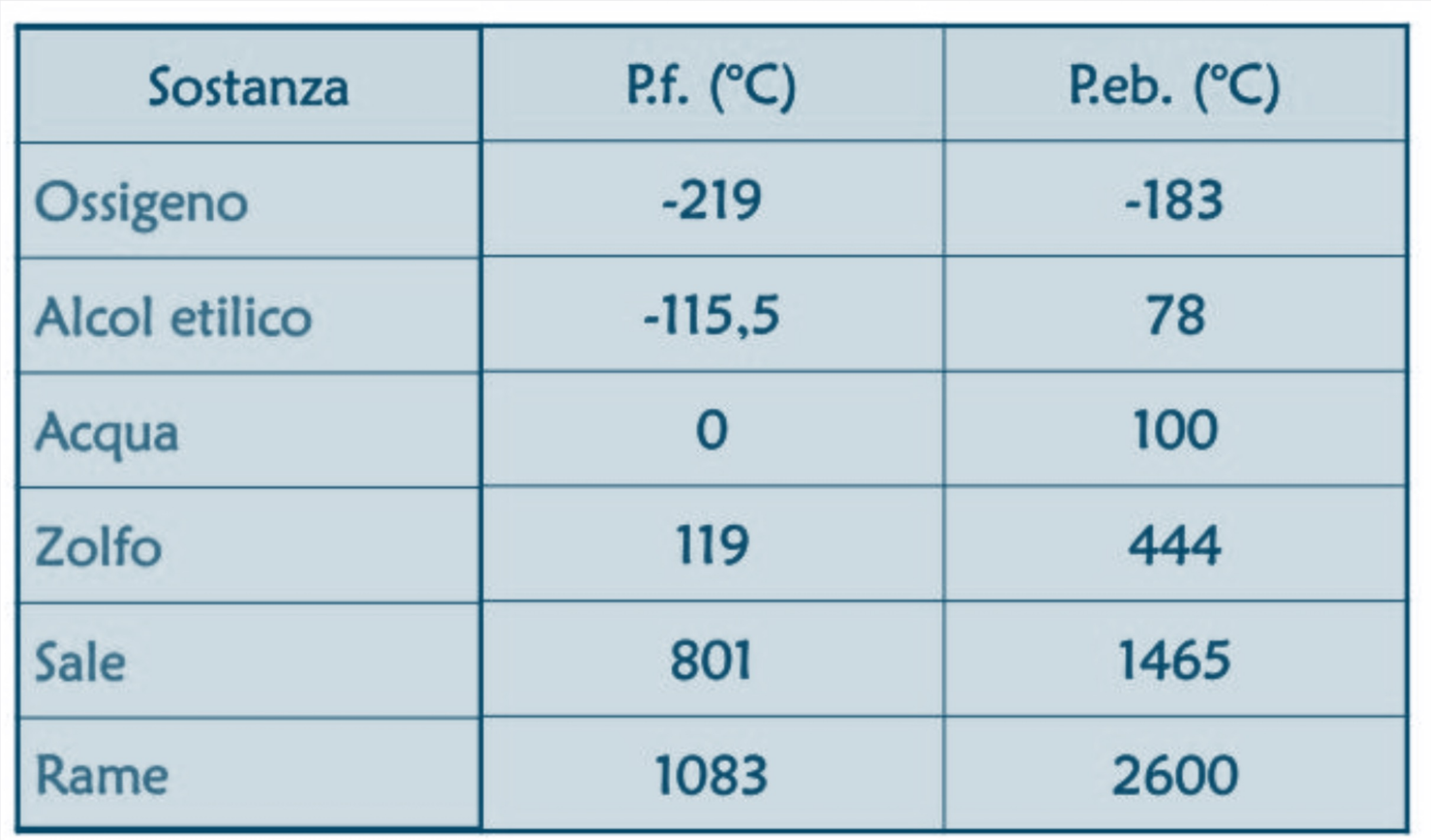
Nella struttura chimica sono scritte le proprietà e la reattività delle sostanze



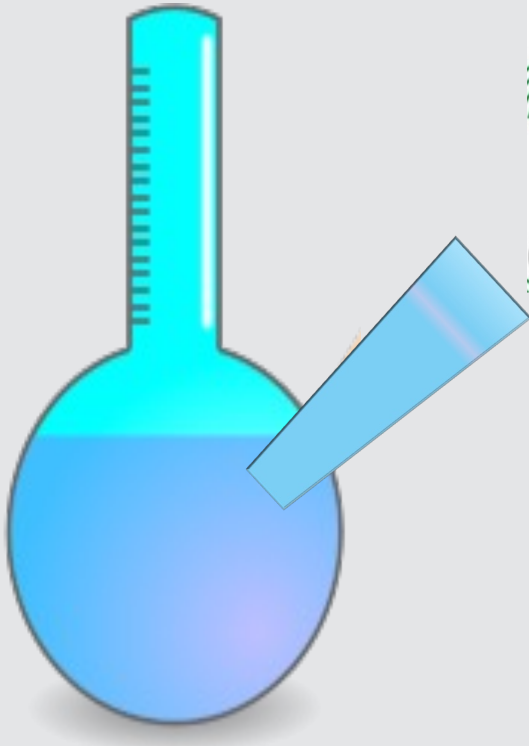


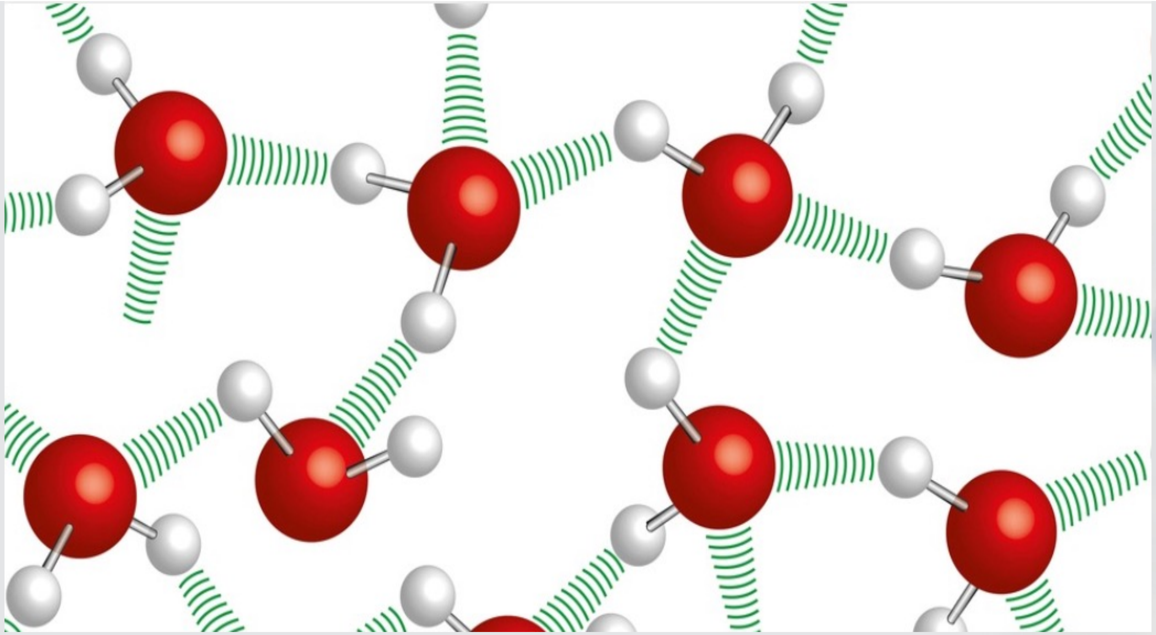


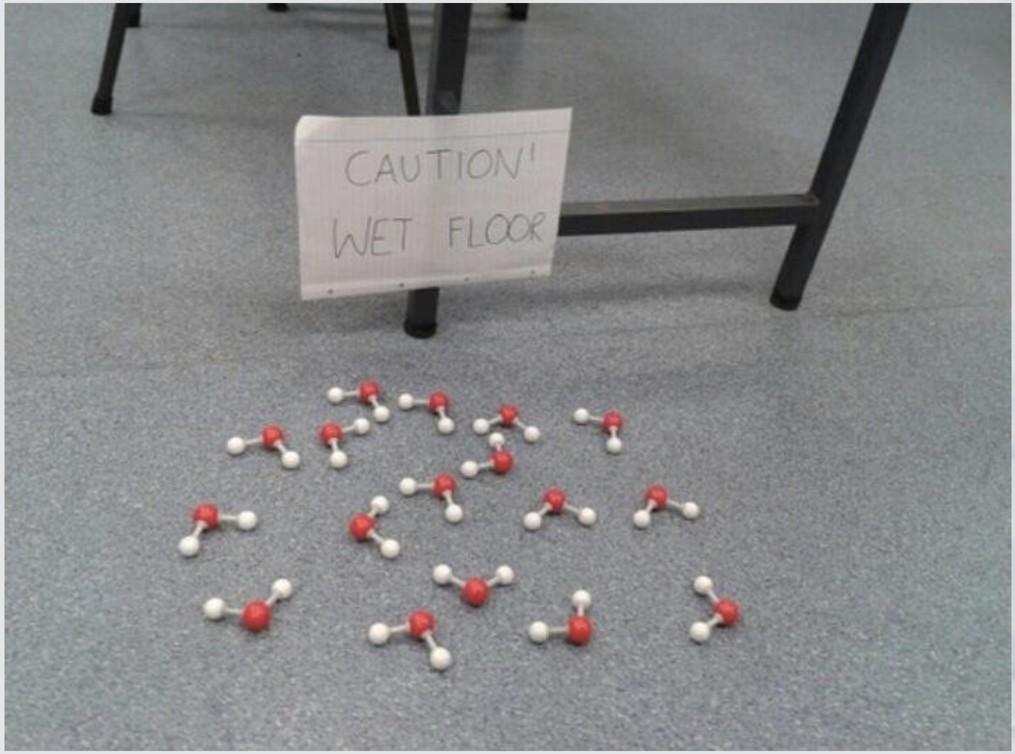




Sostanza	P.f. (°C)	P.eb. (°C)
Ossigeno	-219	-183
Alcol etilico	-115,5	78
Acqua	0	100
Zolfo	119	444
Sale	801	1465
Rame	1083	2600

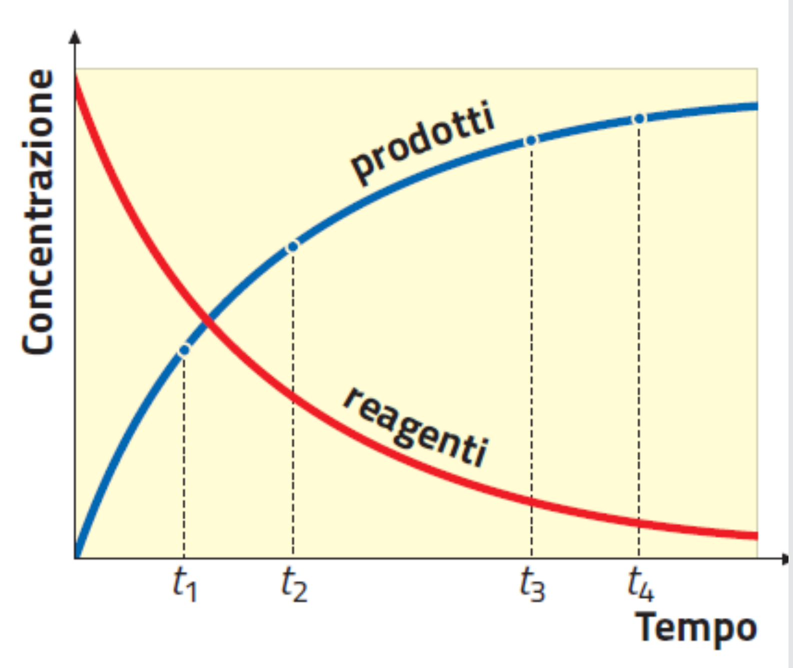


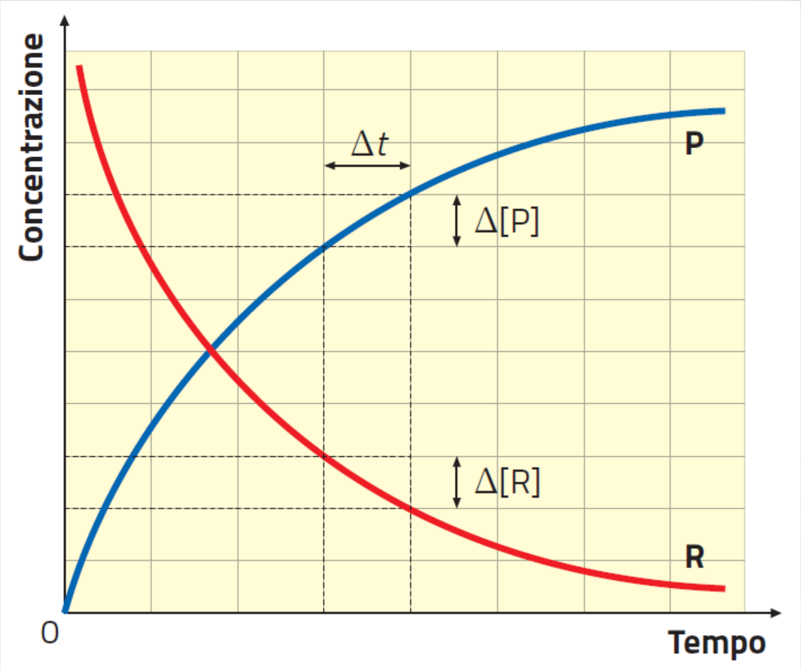



CAUTION!
WET FLOOR

E il tempo?

$$aA + bB \rightarrow cC + dD$$





$$v = -\frac{\Delta[R]}{\Delta t}$$

$$v = \frac{\Delta[P]}{\Delta t}$$

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

$$v = k[A]^x\,[B]^y$$

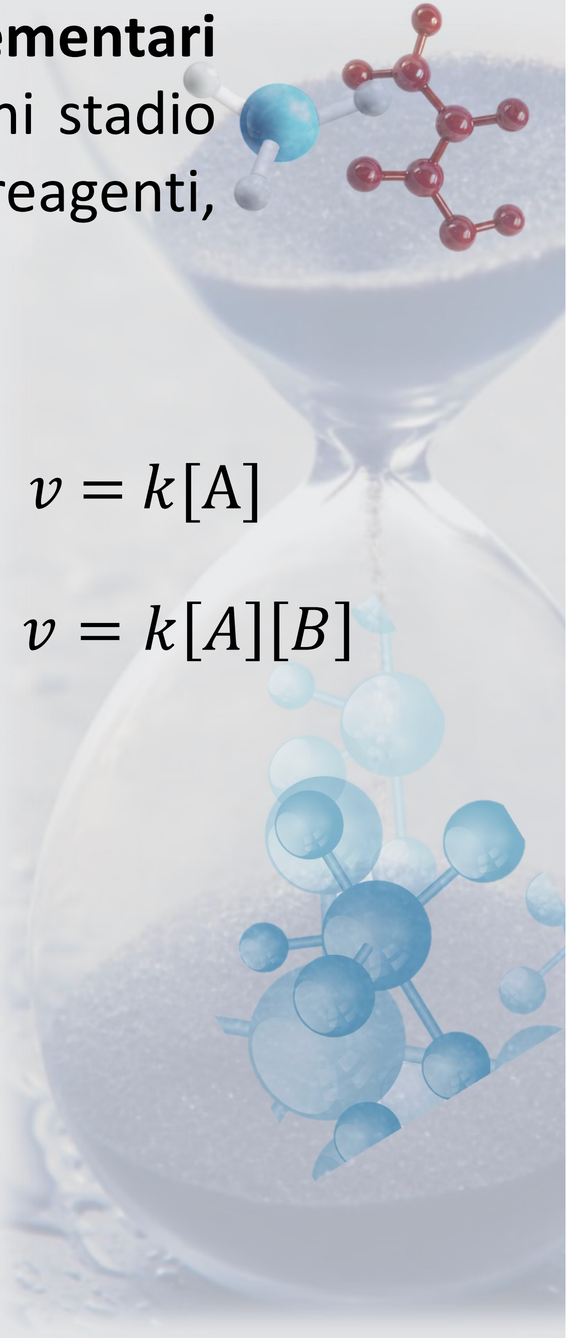
La velocità di reazione dipende dalla:

- Natura dei reagenti
- Concentrazione dei reagenti
- Temperatura di reazione
- Presenza di eventuali catalizzatori
- Superficie dell'interfaccia (se la reazione avviene tra reagenti in due fasi diverse)

Il **meccanismo di reazione** è la sequenza di **stadi elementari** attraverso cui i reagenti si trasformano nei prodotti. Ogni stadio elementare coinvolge un numero definito di particelle reagenti, definito **molecolarità**.

Reazione unimolecolare (molecolarità = 1) A→P $v = k[\mathrm{A}]$

Reazione bimolecolare (molecolarità = 2) $A + B \rightarrow P$ $v = k[A][B]$



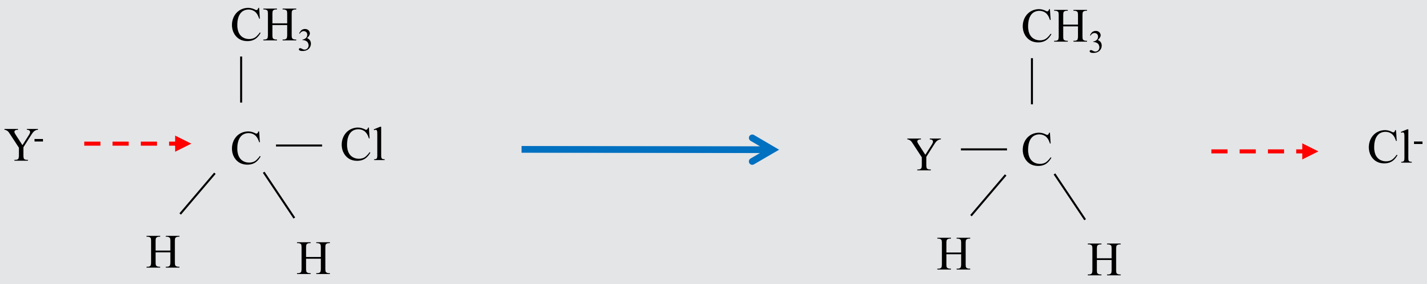
$$^{\delta^+}R - X^{\delta^-} \quad + \quad Y^- \longrightarrow R - Y \quad + \quad X^-$$

Caso 1)

1° stadio: $R - X \leftrightarrows R^{\oplus} + X^-$

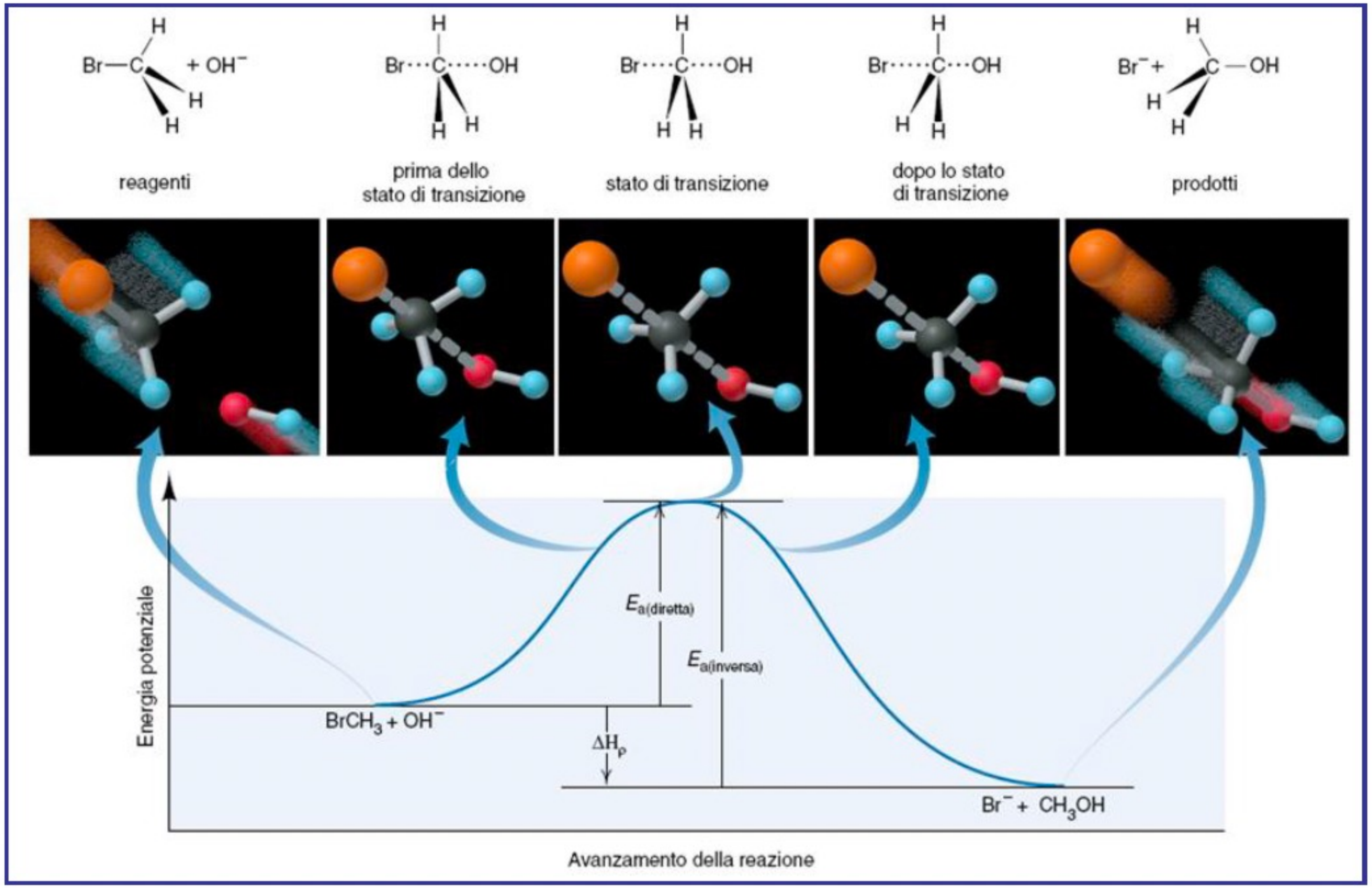
2° stadio: $R^{\oplus} + Y^- \rightarrow R - Y$

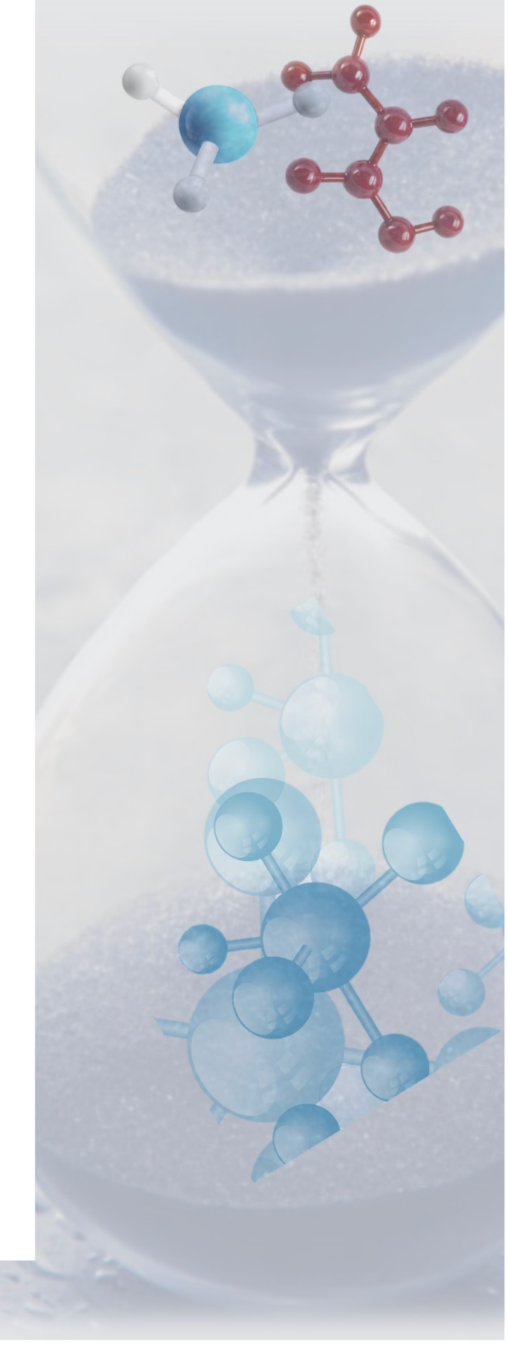
Caso 2)


Y-
CH3
C
Cl
H
H
CH3
Y
C
H
H
Cl-

Stato di transizione
Diagramma dell'energia di reazione

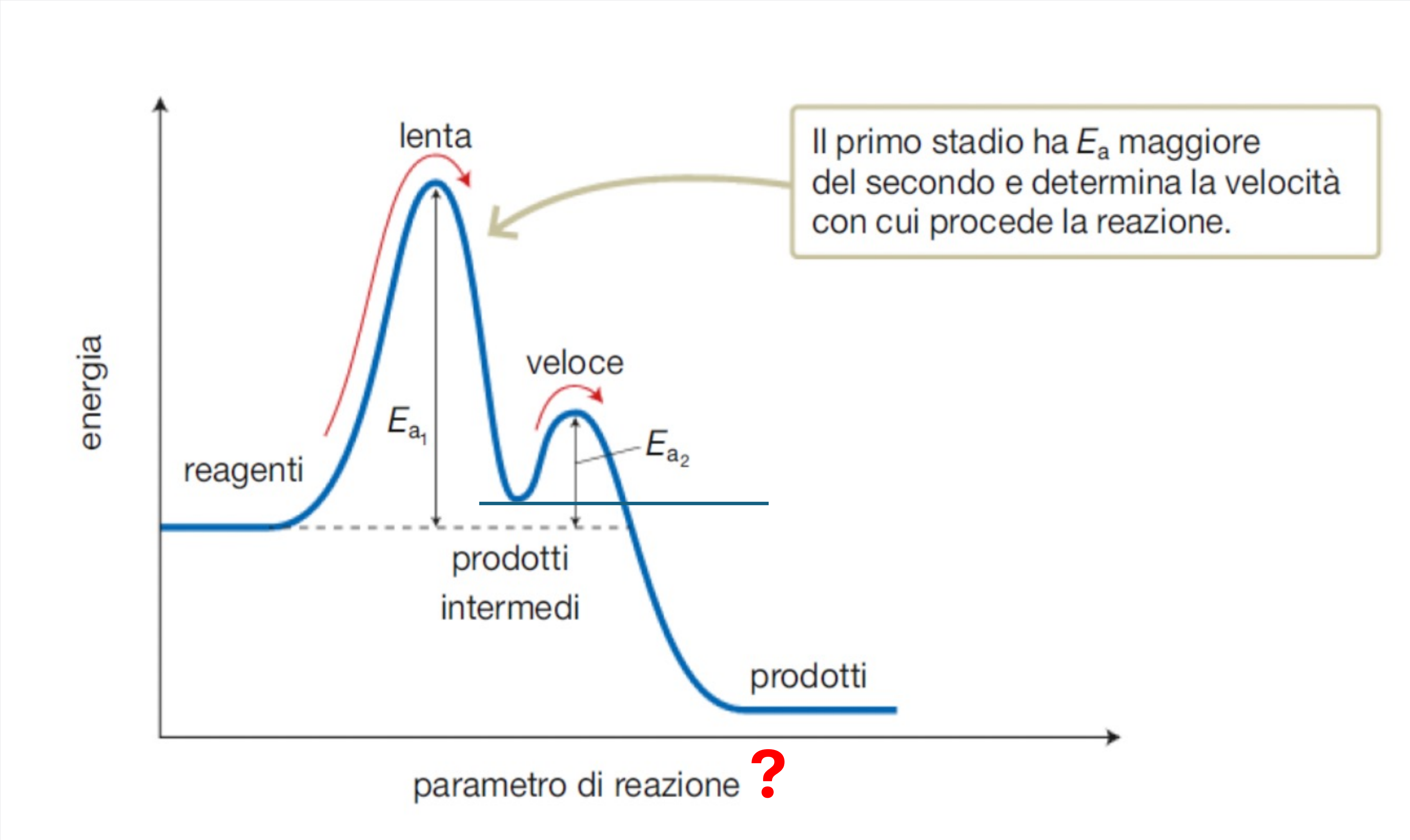
$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$


reagenti
prima dello stato di transizione
stato di transizione
dopo lo stato di transizione
prodotti
Br—C + OH⁻
Br···C·····OH
Br⁻ + C—OH
H
Energia potenziale
$BrCH_3 + OH^-$
$E_{a(diretta)}$
$E_{a(inversa)}$
ΔH_p
$Br^- + CH_3OH$
Avanzamento della reazione

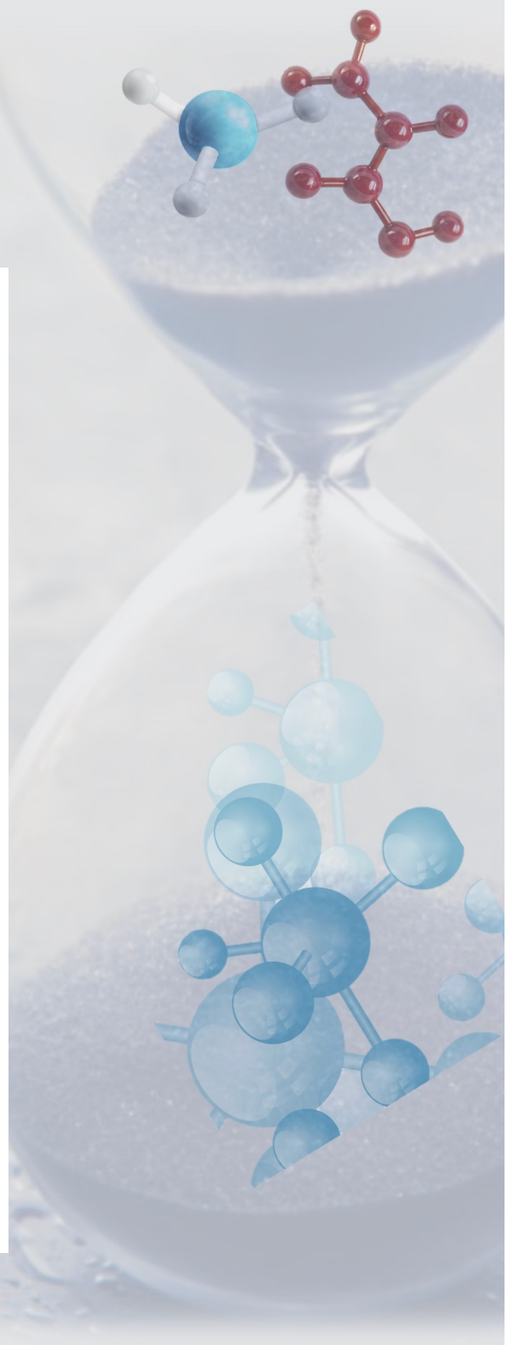


R → P

R → I → P

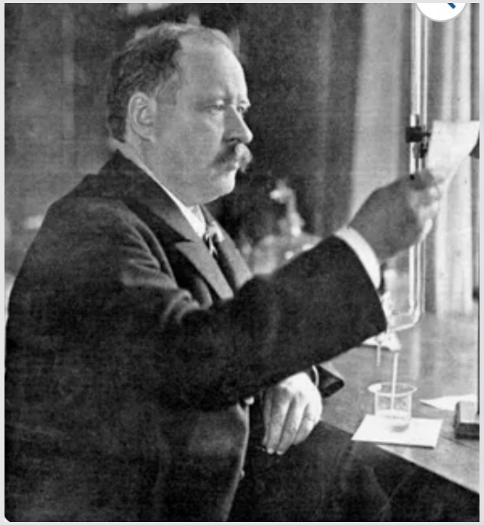


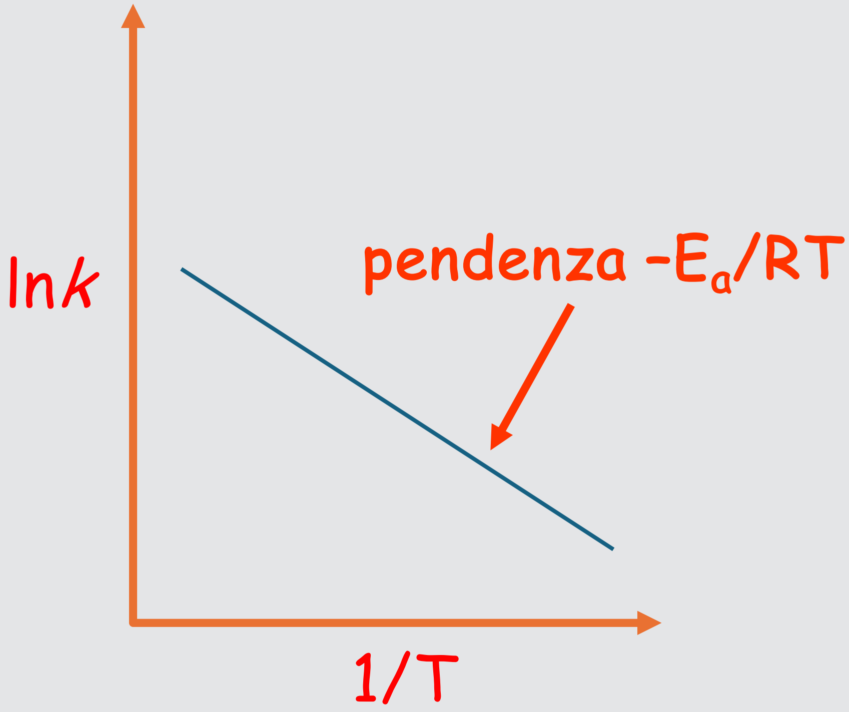
Il primo stadio ha E_a maggiore del secondo e determina la velocità con cui procede la reazione.

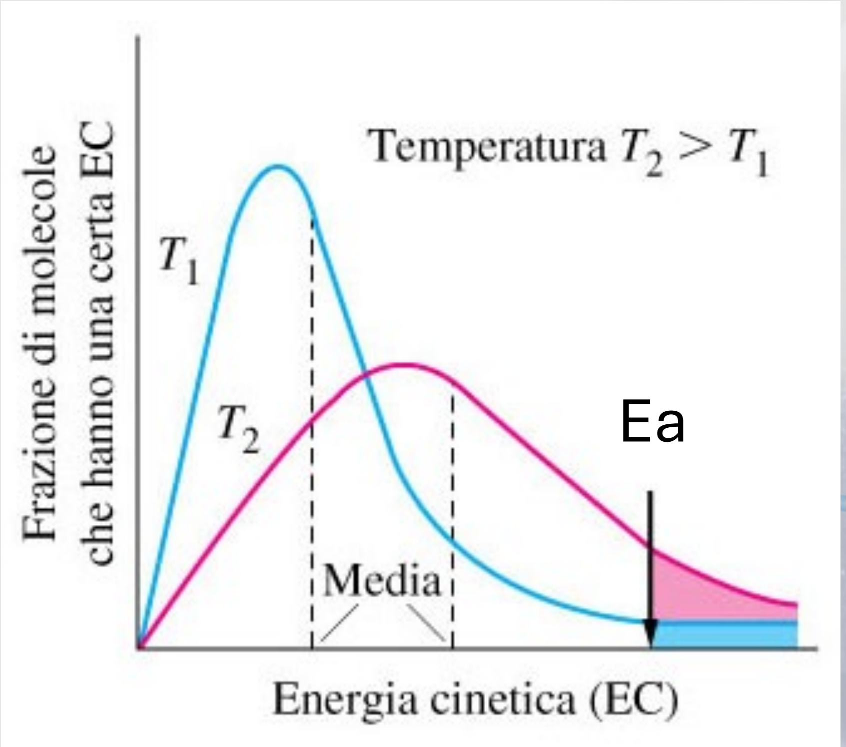


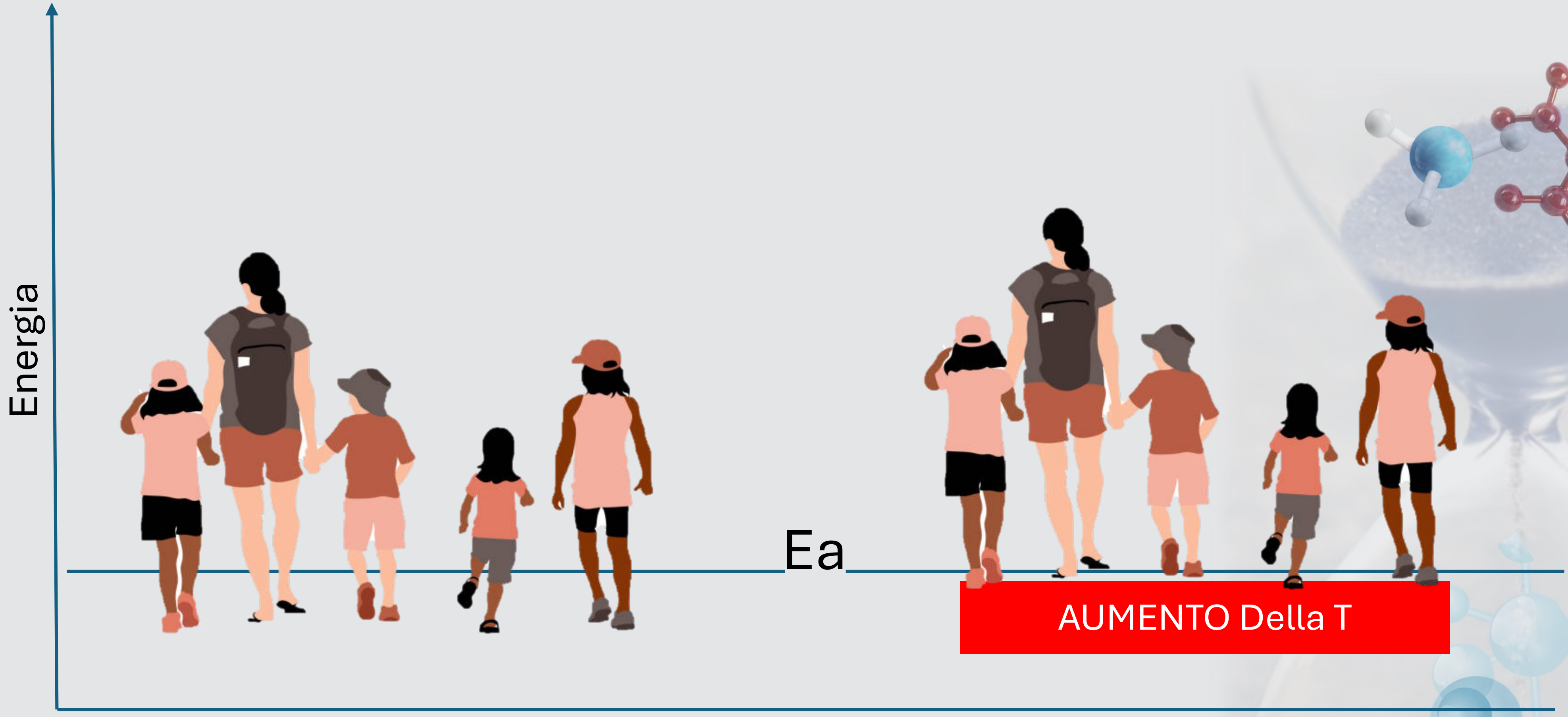
$$\ln \mathbf{k} = \ln \mathbf{A} - \frac{\mathbf{E_a}}{\mathbf{RT}}$$

$$\log \mathbf{k} = \log \mathbf{A} - \frac{\mathbf{E_a}}{\mathbf{2{,}303\ RT}}$$

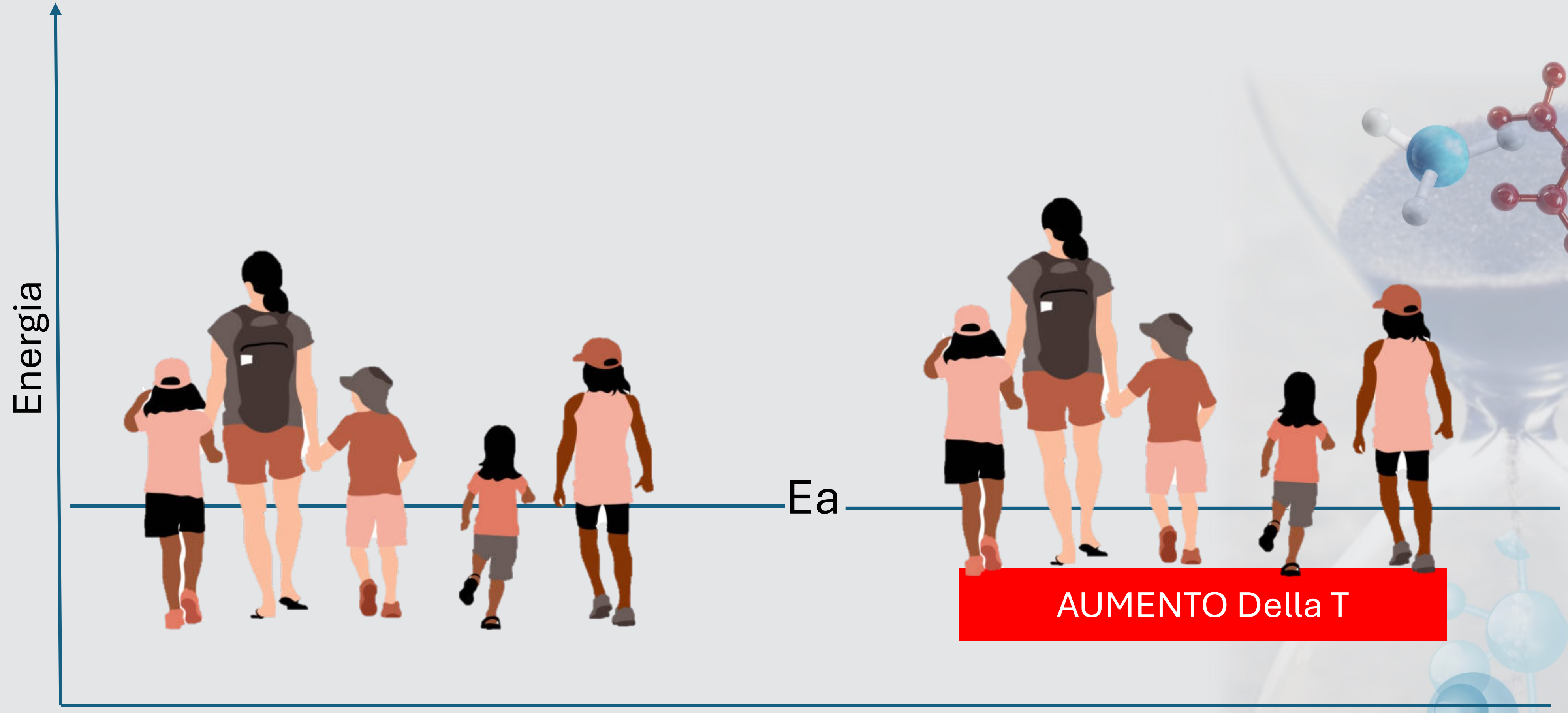




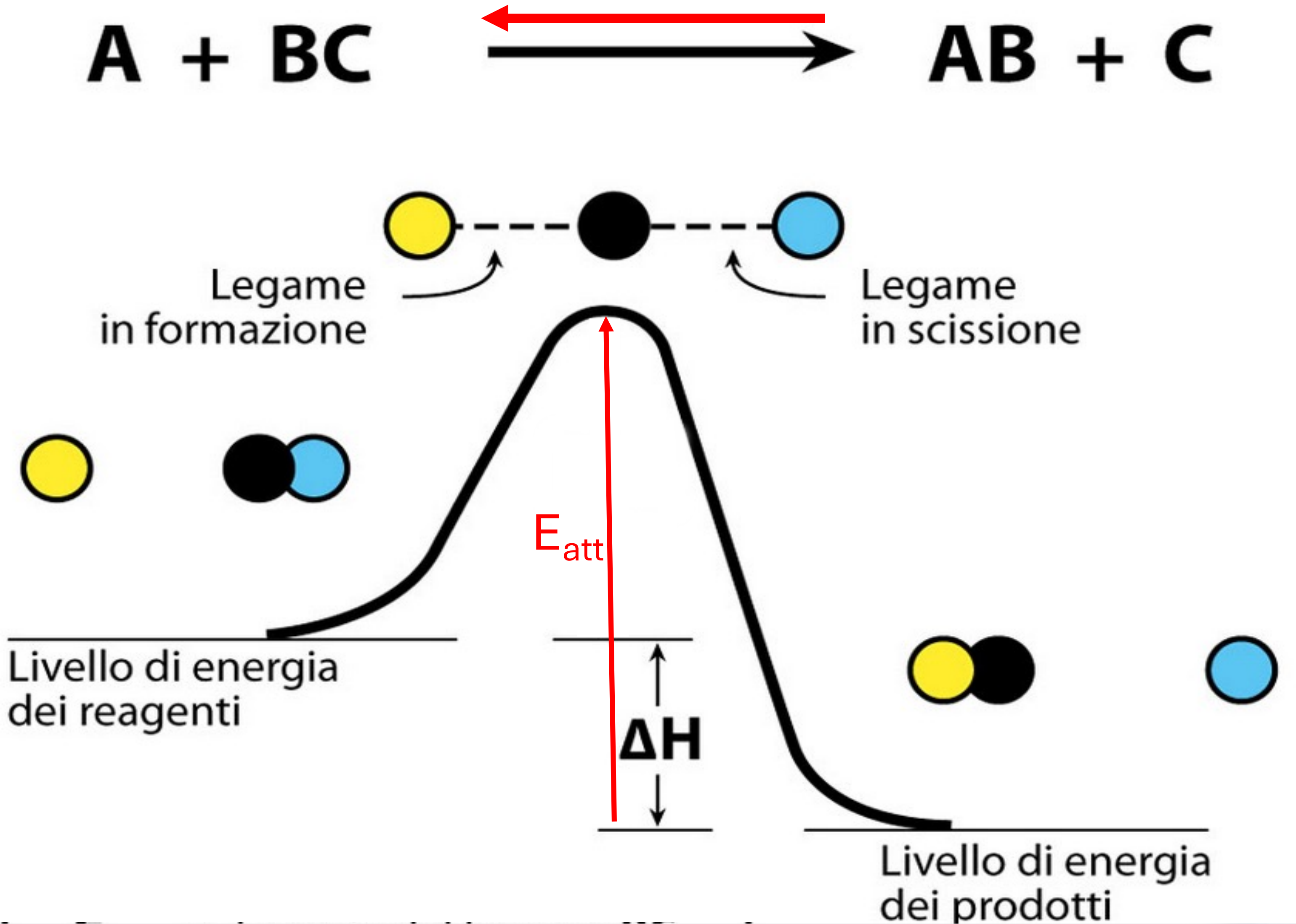




AUMENTO Della T


Energia
Ea
AUMENTO Della T

SVOLGIMENTO DI UNA REAZIONE CHIMICA



$\mathrm{A} + \mathrm{BC} \rightleftarrows \mathrm{AB} + \mathrm{C}$

Legame in formazione

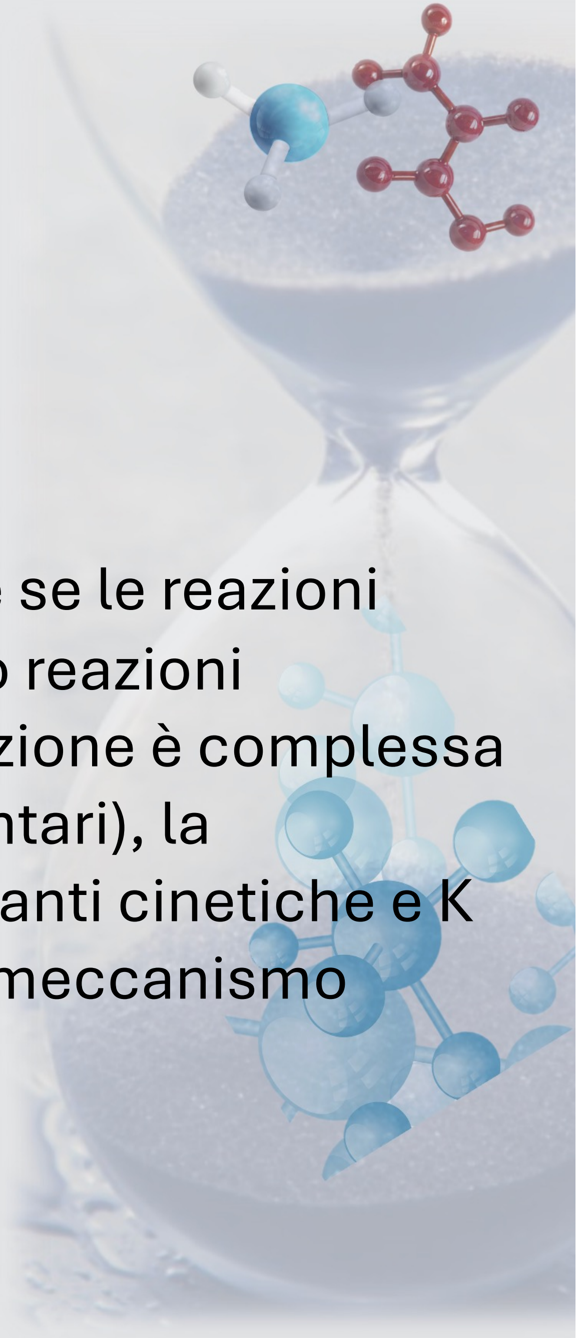
Legame in scissione

E_{att}

ΔH

Livello di energia dei reagenti

Livello di energia dei prodotti



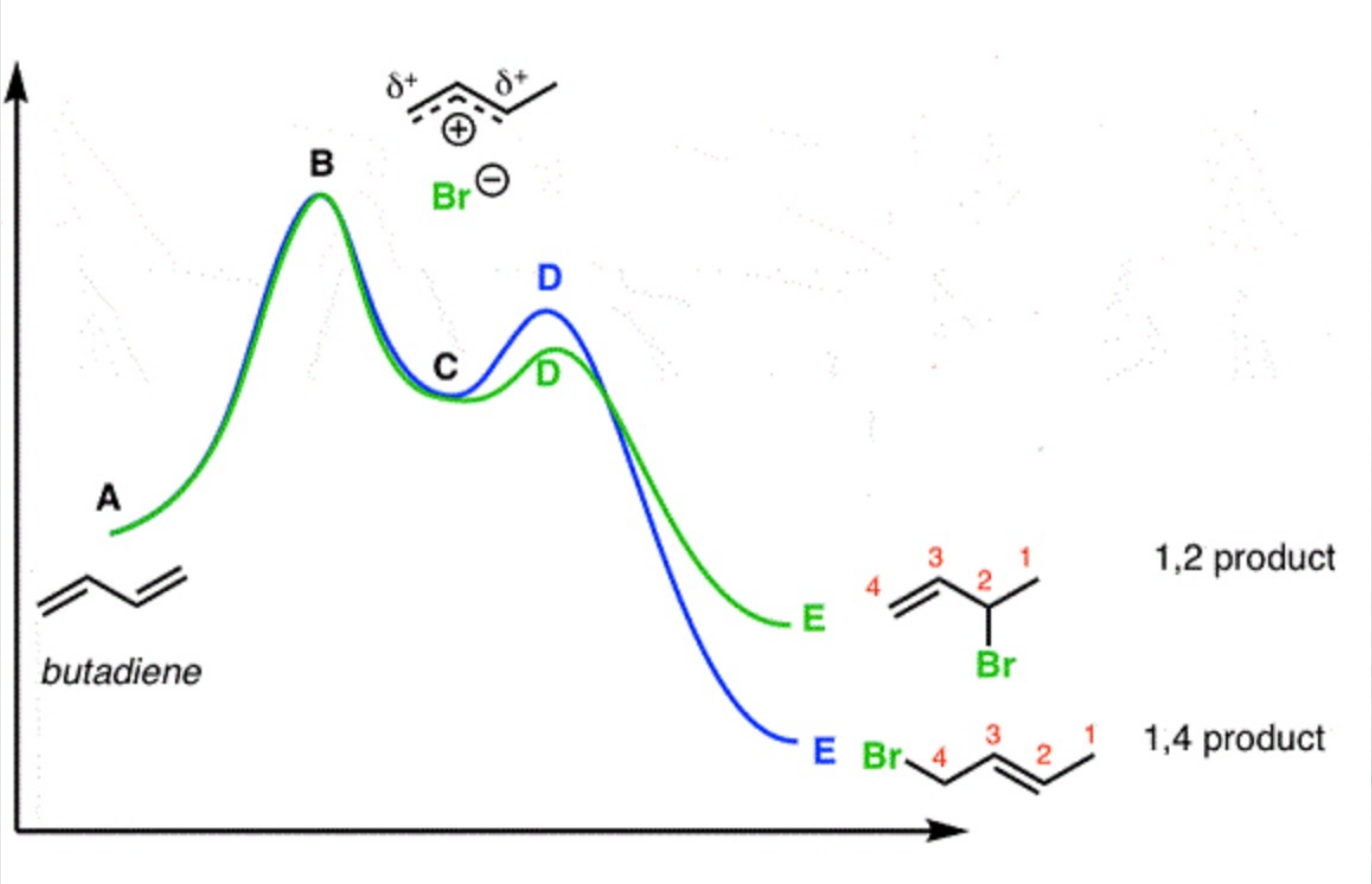
$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

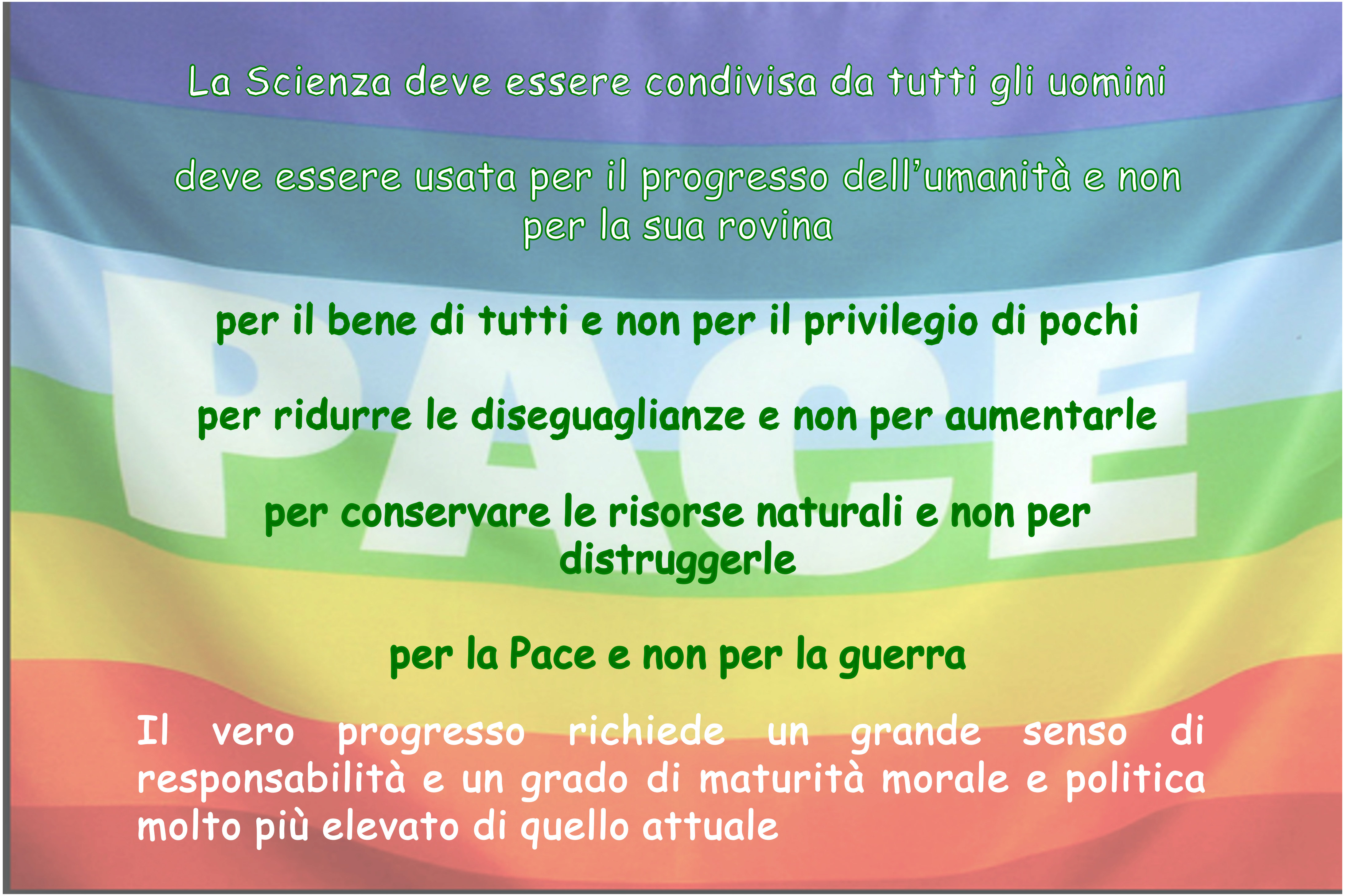
$$v_1 = k_1[\mathrm{A}]\,[\mathrm{B}] \qquad v_2 = k_2[\mathrm{C}]\,[\mathrm{D}]$$

$$k_1[\mathrm{A}]\,[\mathrm{B}] = k_2[\mathrm{C}]\,[\mathrm{D}]$$

$$\frac{k_1}{k_2} = \frac{[\mathrm{C}]\,[\mathrm{D}]}{[\mathrm{A}]\,[\mathrm{B}]} = K$$

questa relazione vale se le reazioni diretta e inversa sono reazioni elementari. Se la reazione è complessa (più stadi non elementari), la connessione tra costanti cinetiche e K richiede l’analisi del meccanismo completo


δ+
δ+
+
Br −
B
D
C
D
A
E
E
butadiene
4
3
2
1
Br
1,2 product
Br
4
3
2
1
1,4 product



La Scienza deve essere condivisa da tutti gli uomini

deve essere usata per il progresso dell'umanità e non per la sua rovina

per il bene di tutti e non per il privilegio di pochi

per ridurre le diseguaglianze e non per aumentarle

per conservare le risorse naturali e non per distruggerle

per la Pace e non per la guerra

Il vero progresso richiede un grande senso di responsabilità e un grado di maturità morale e politica molto più elevato di quello attuale

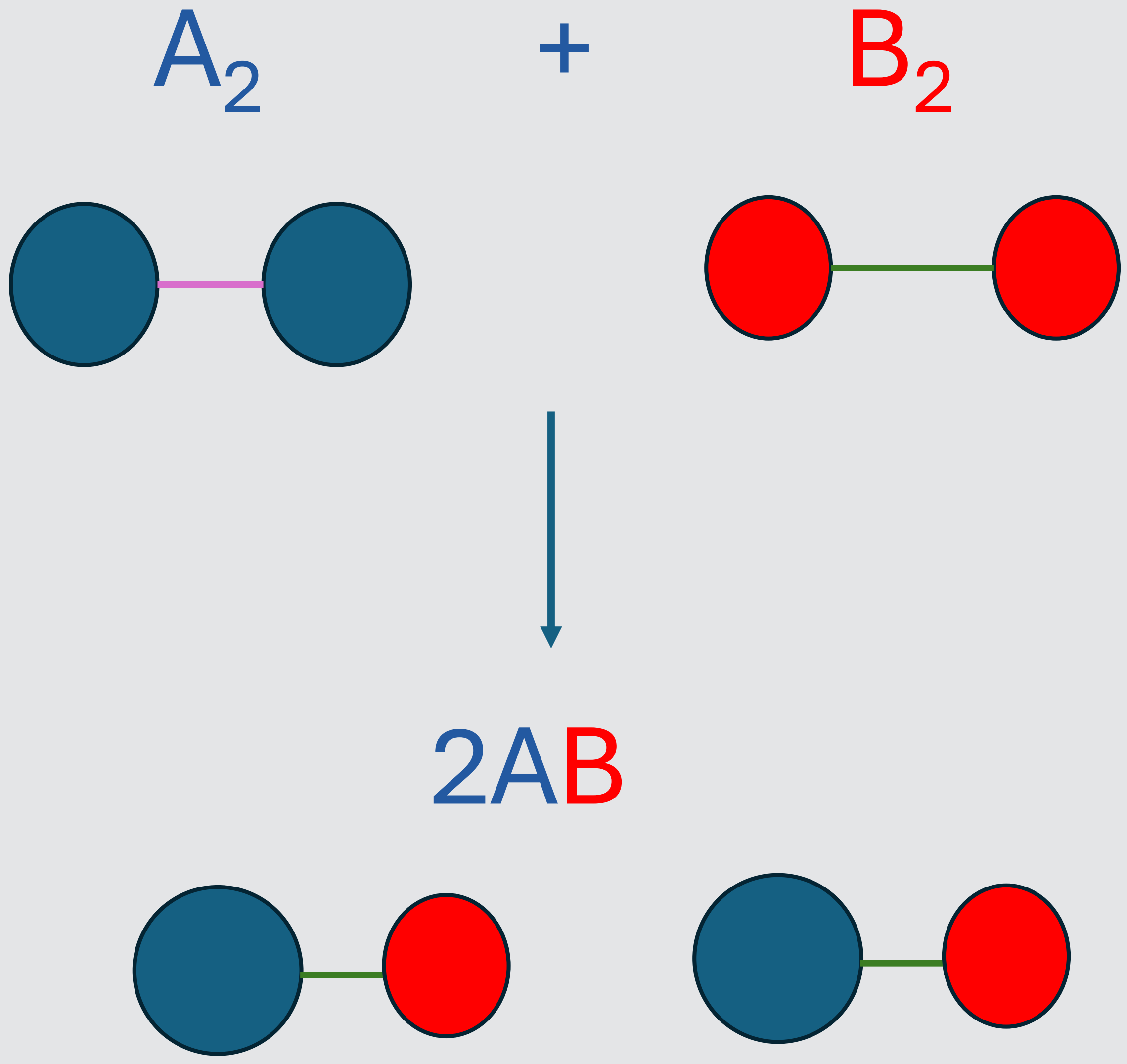
GRAZIE

«Il futuro appartiene a coloro che credono nella bellezza dei propri sogni»

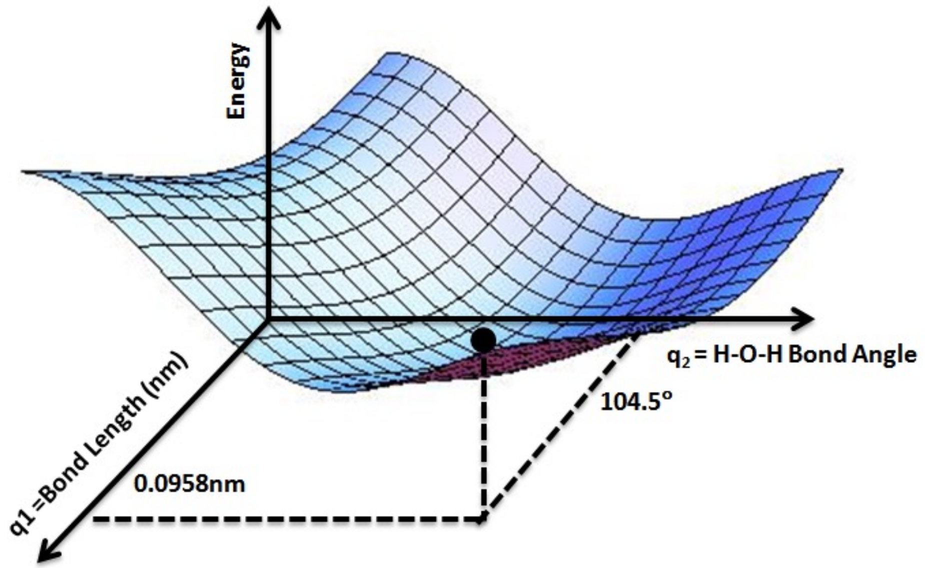
Eleanor Roosevelt

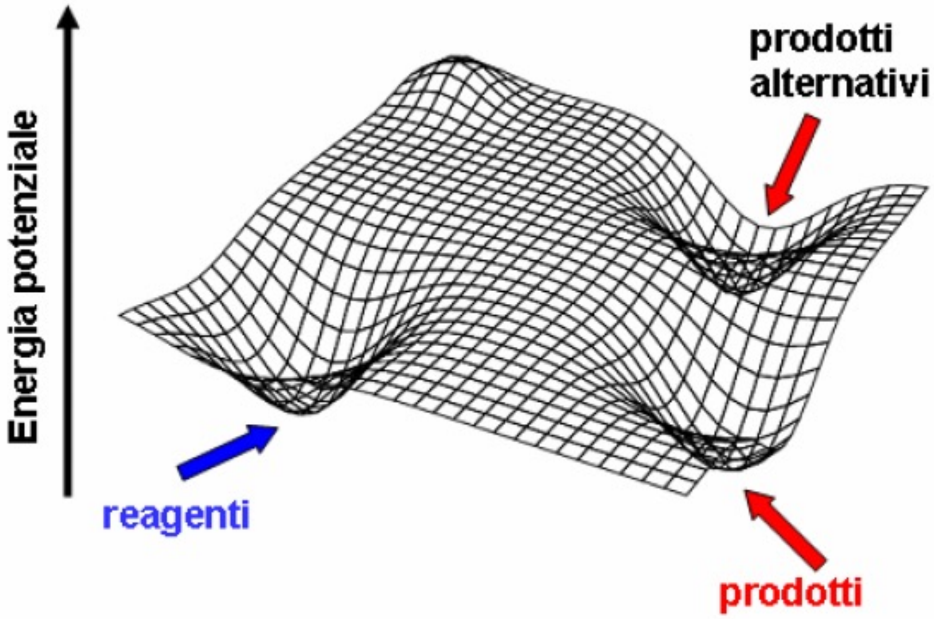
https://www.youtube.com/watch?v=dQGreQyoXxI

REAZIONI



$$A_2 + B_2 \longrightarrow 2AB$$


Energy
q_2 = H-O-H Bond Angle
104.5°
q1 =Bond Length (nm)
0.0958nm


Energia potenziale
prodotti alternativi
reagenti
prodotti