ESALQ - Escola Superior de Agricultura "Luiz de Queiroz"

Bioquímica Animal e de Alimentos

Prof. Severino Matias de Alencar

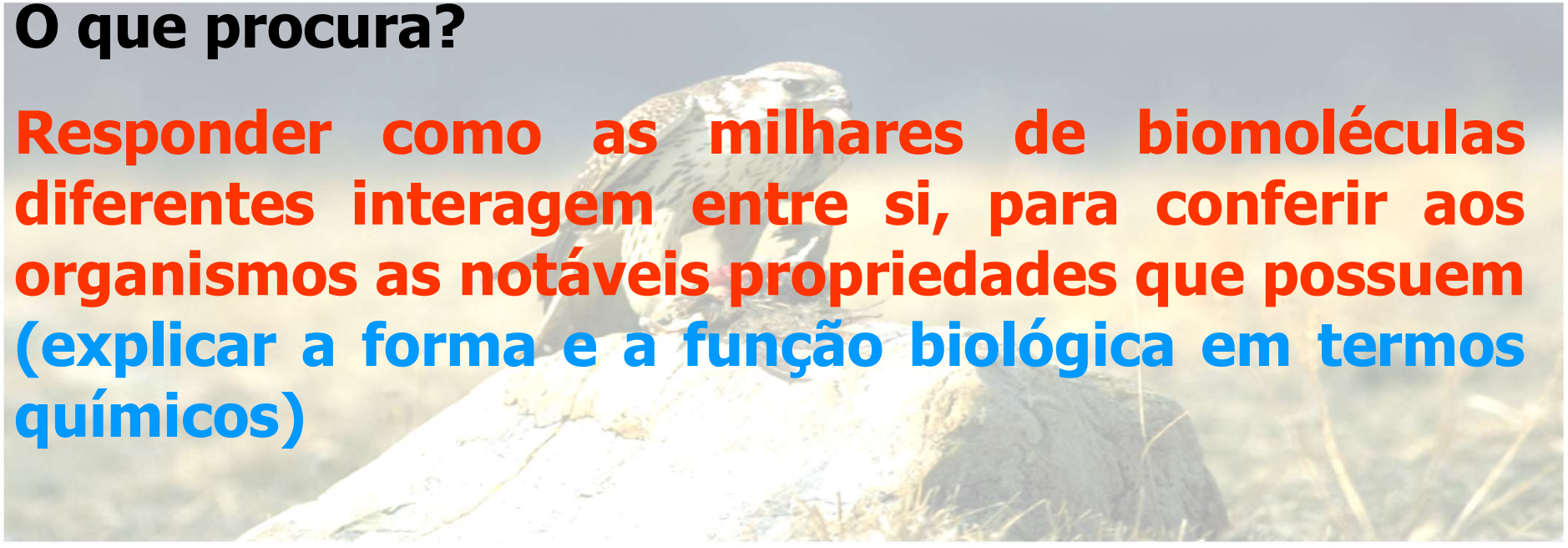
Introdução

Bioquímica: estudo da base molecular da vida

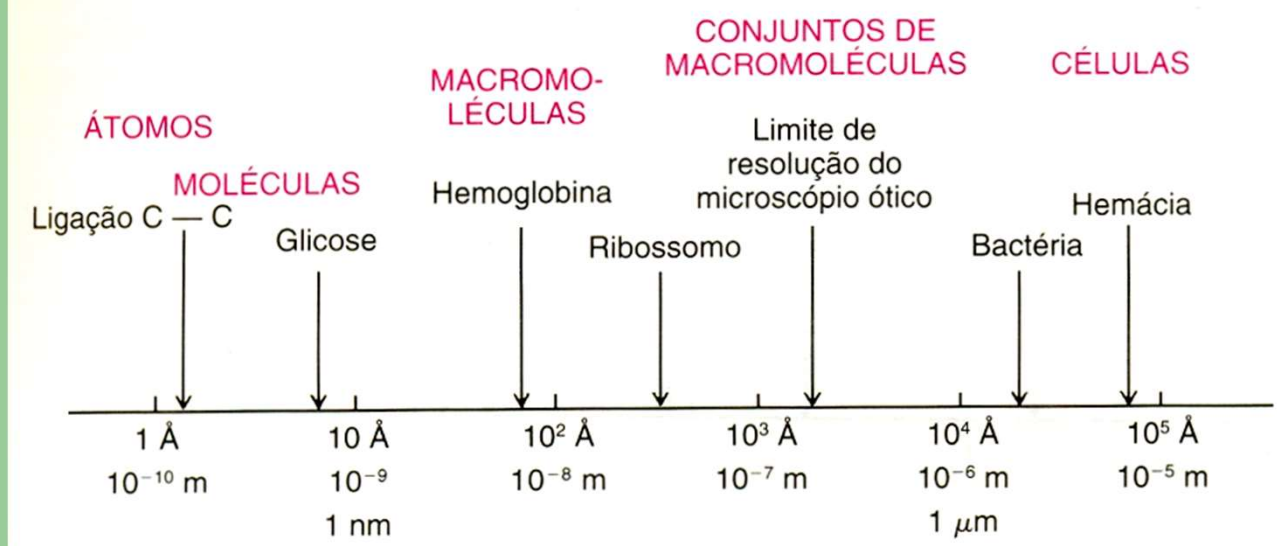
Biomoléculas isoladas: são destituídas de vida e obedecem a todas as leis físicas e químicas da matéria inanimada

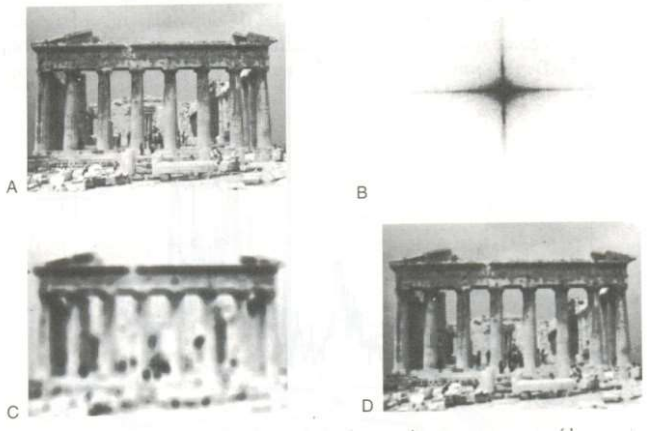
O que procura?

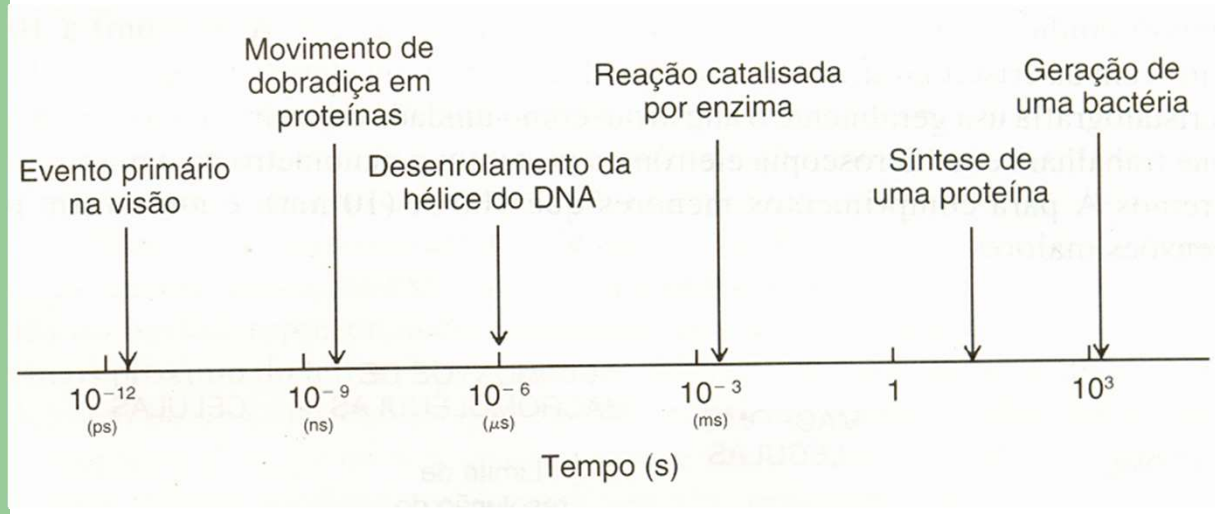
Responder como as milhares de biomoléculas diferentes interagem entre si, para conferir aos organismos as notáveis propriedades que possuem (explicar a forma e a função biológica em termos químicos)

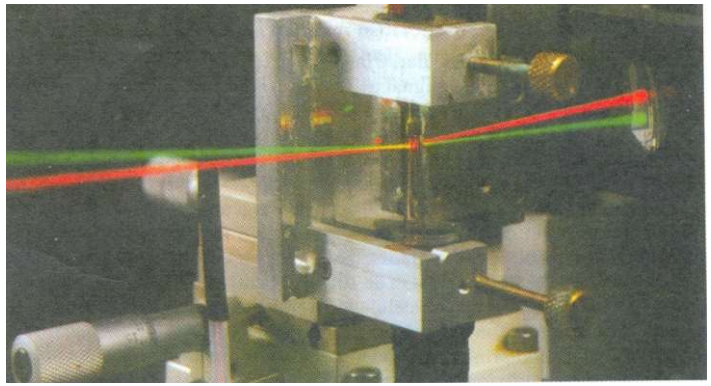


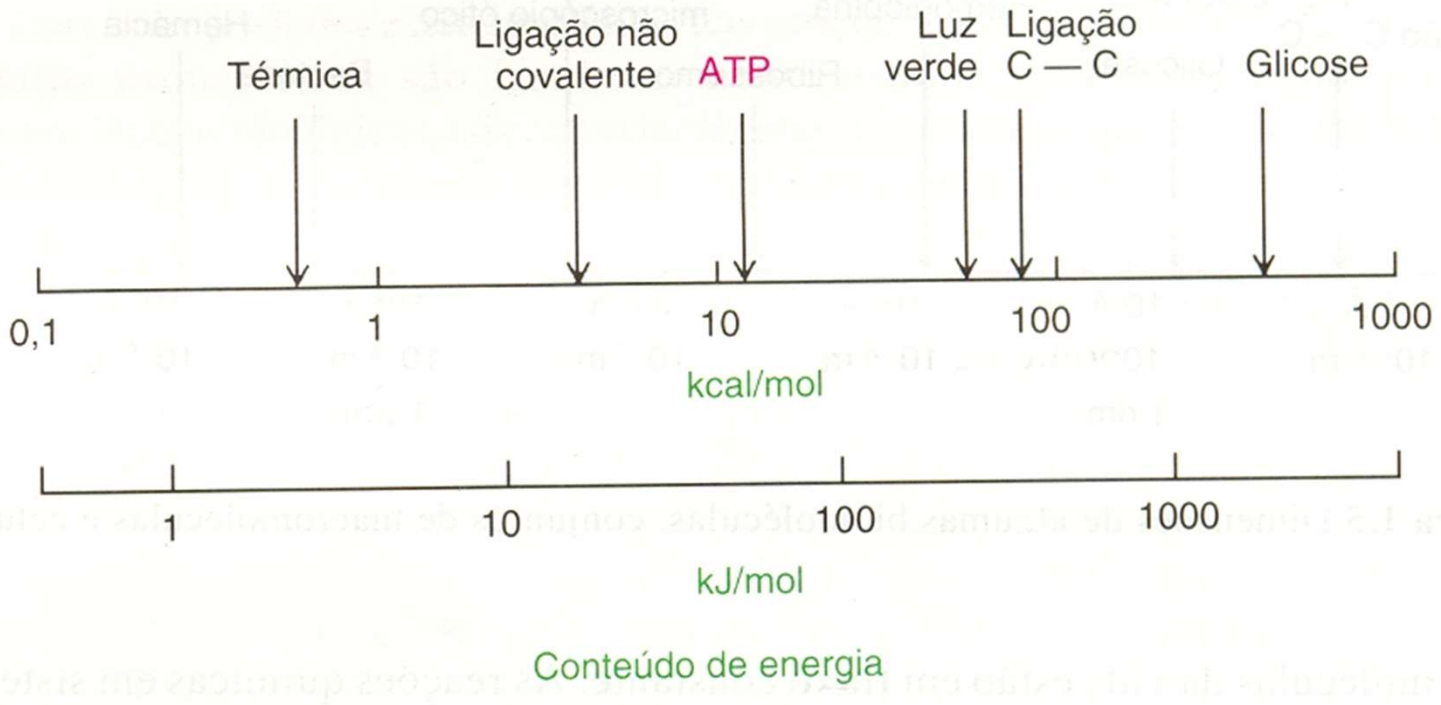
Espaço, Tempo e Energia





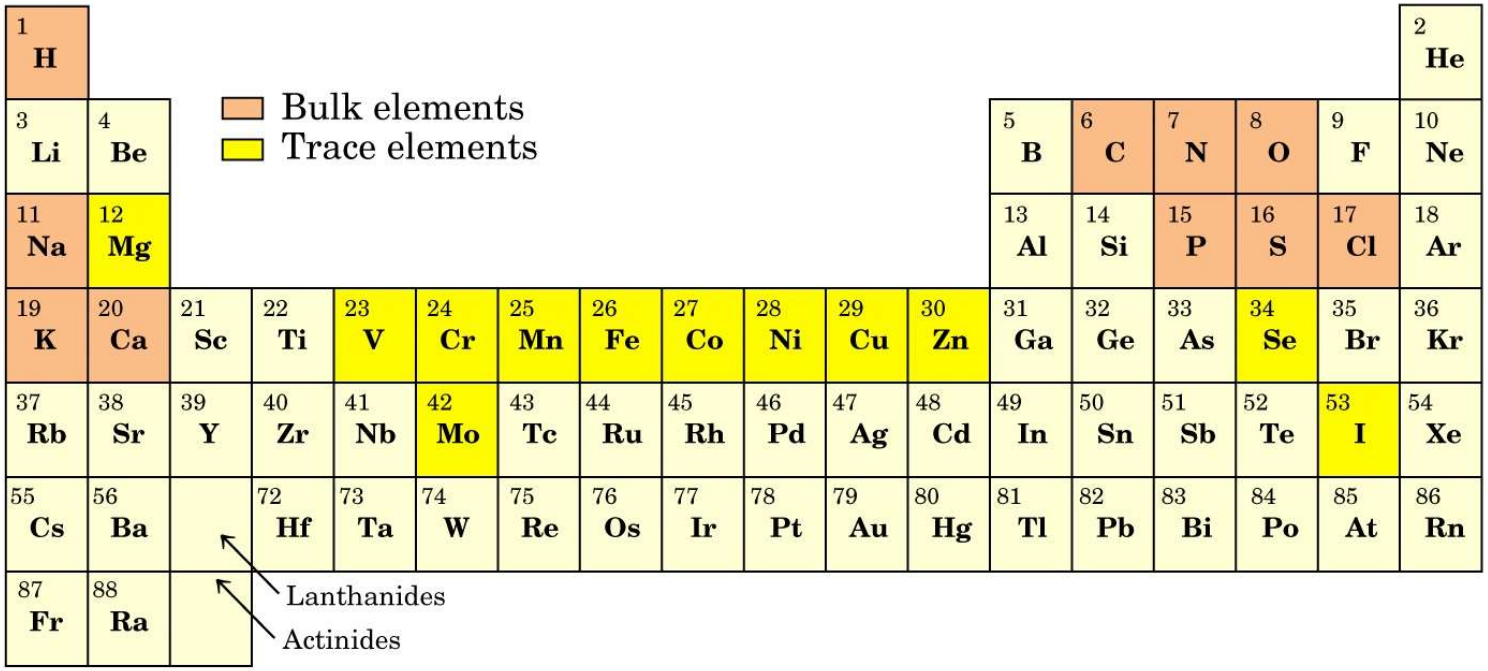





Térmica
Ligação não covalente
ATP
Luz verde
Ligação C — C
Glicose
0,1
1
10
100
1000
kcal/mol
1
10
100
1000
kJ/mol
Conteúdo de energia

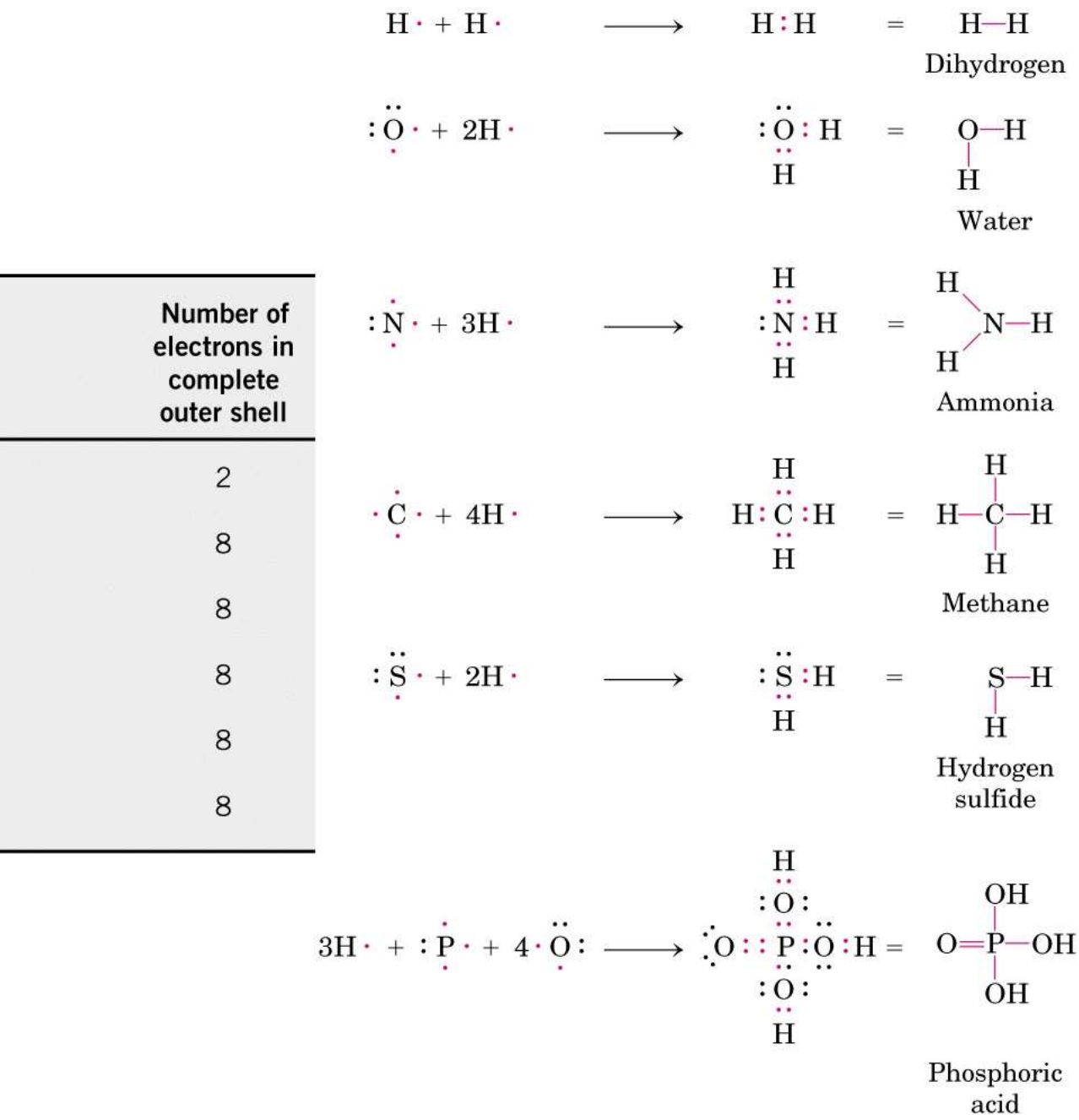
Biomoléculas

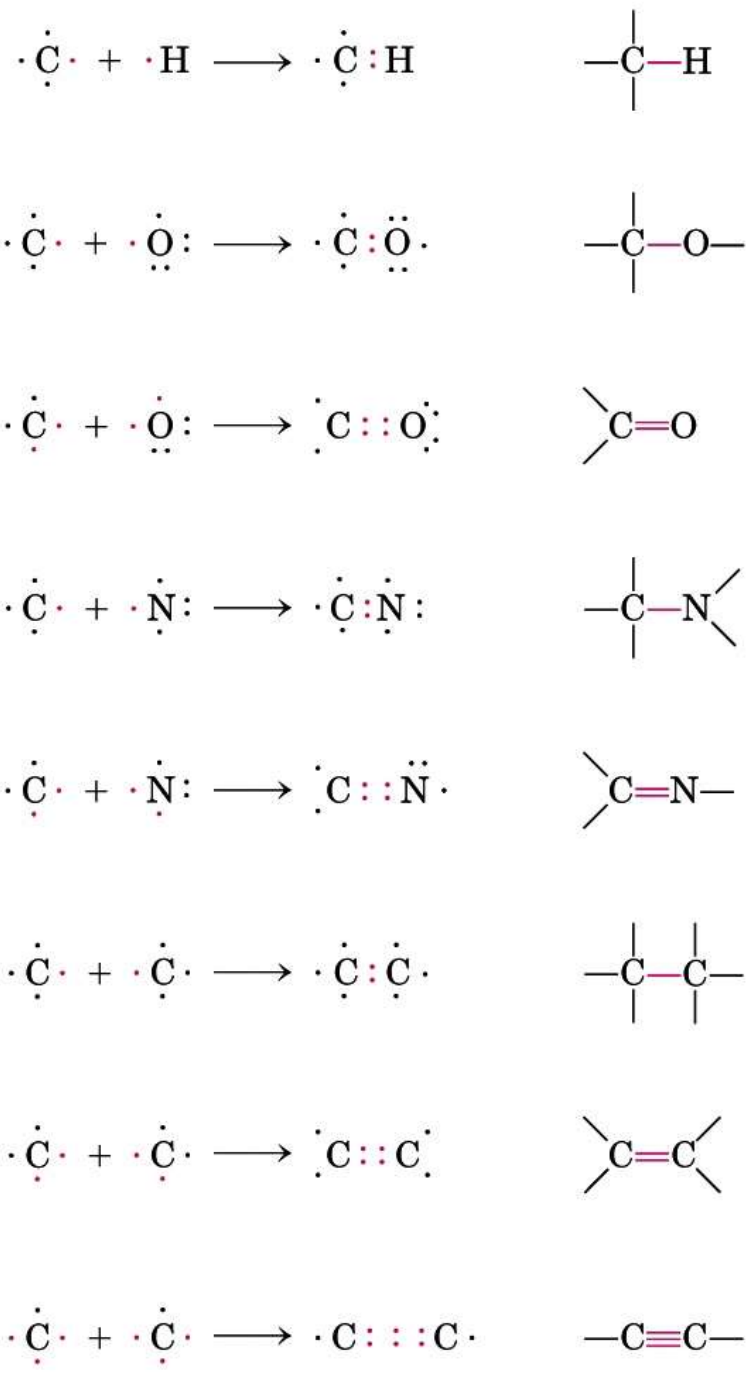
(Compostos do carbono)

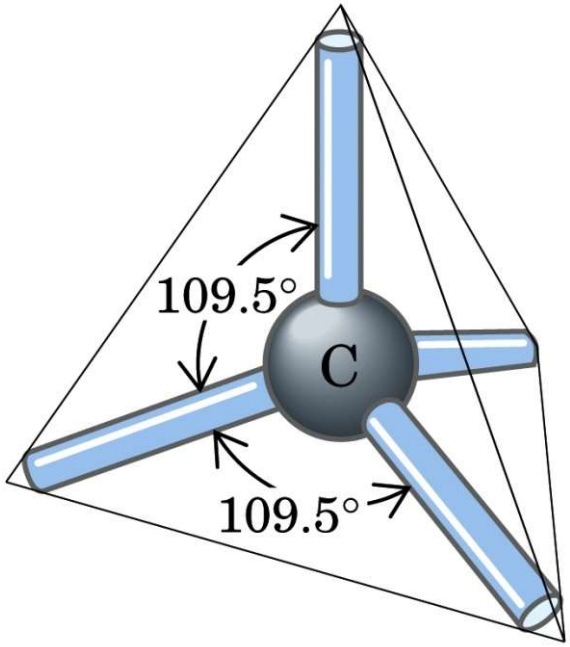


1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra																

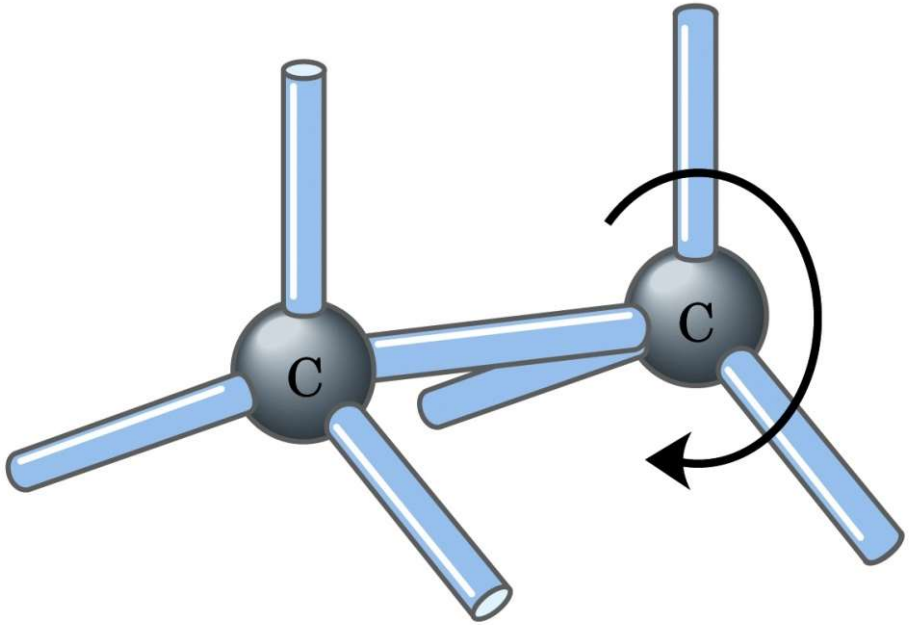
Atom	Number of unpaired electrons (in red)	Number of electrons in complete outer shell
H·	1	2
:Ö·	2	8
:N·	3	8
·C·	4	8
:S·	2	8
:P·	3	8



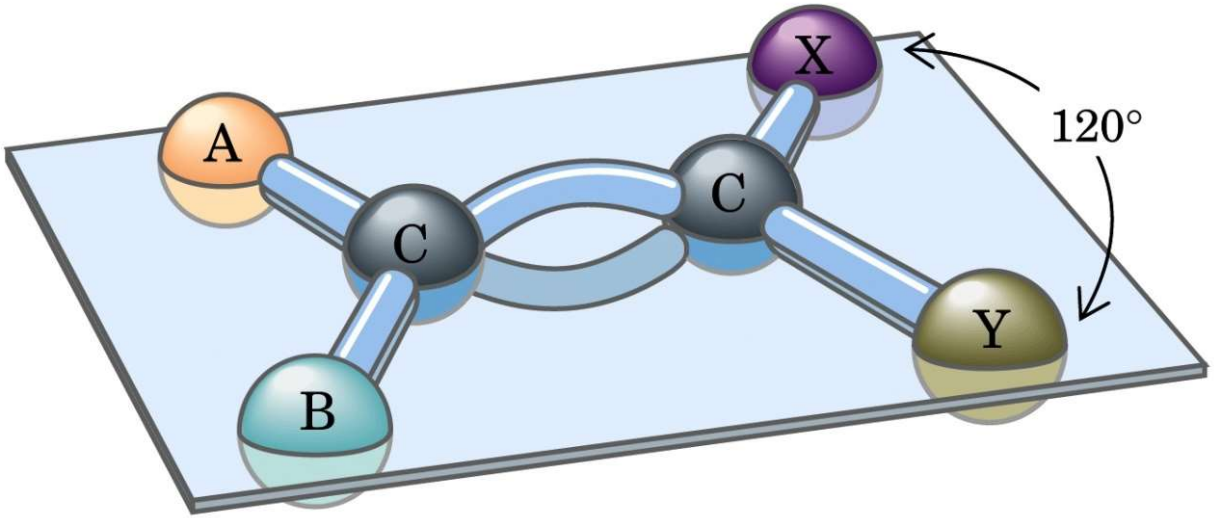




(a)



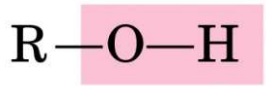
(b)



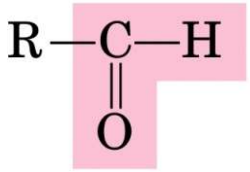
(c)

Alguns grupos funcionais comuns em biomoléculas

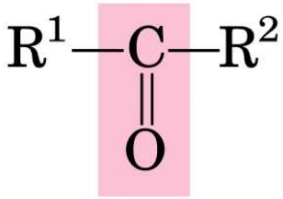
Hydroxyl (alcohol)



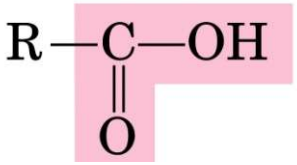
Carbonyl (aldehyde)



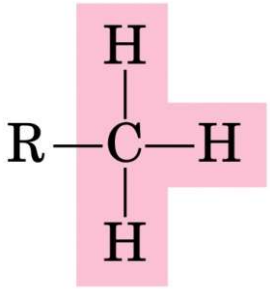
Carbonyl (ketone)



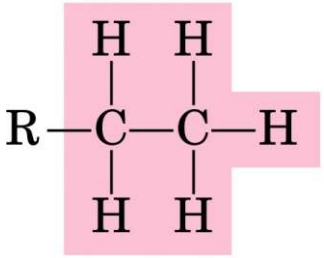
Carboxyl



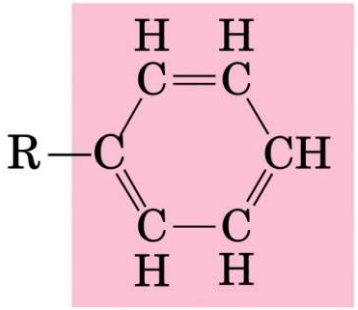
Methyl



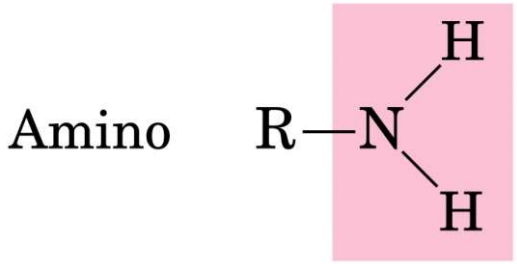
Ethyl



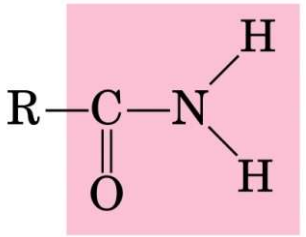
Phenyl



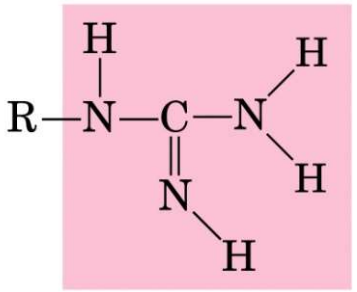
Amino



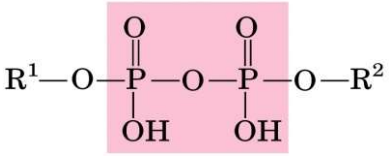
Amido



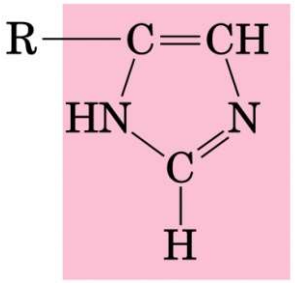
Guanidino



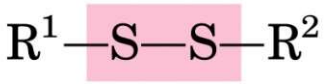
Phosphoanhydride



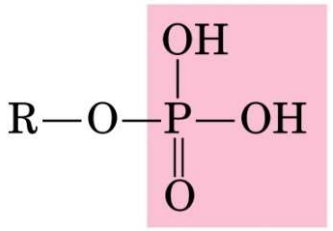
Imidazole



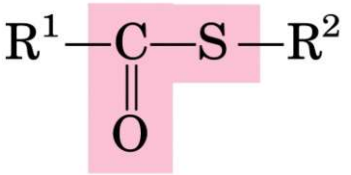
Disulfide



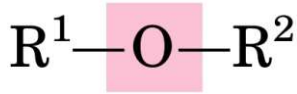
Phosphoryl



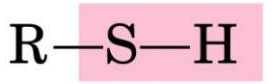
Thioester

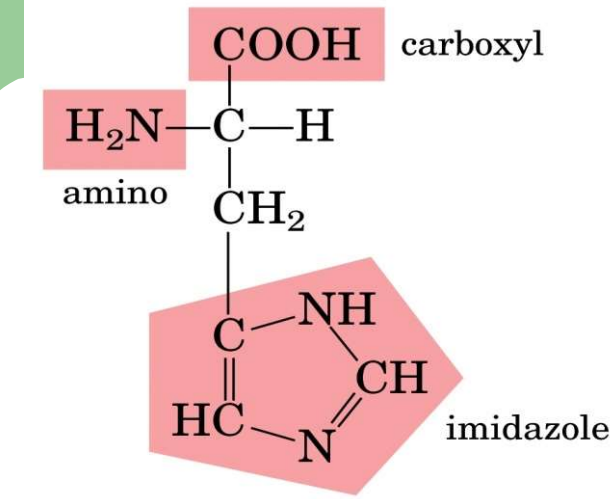


Ether

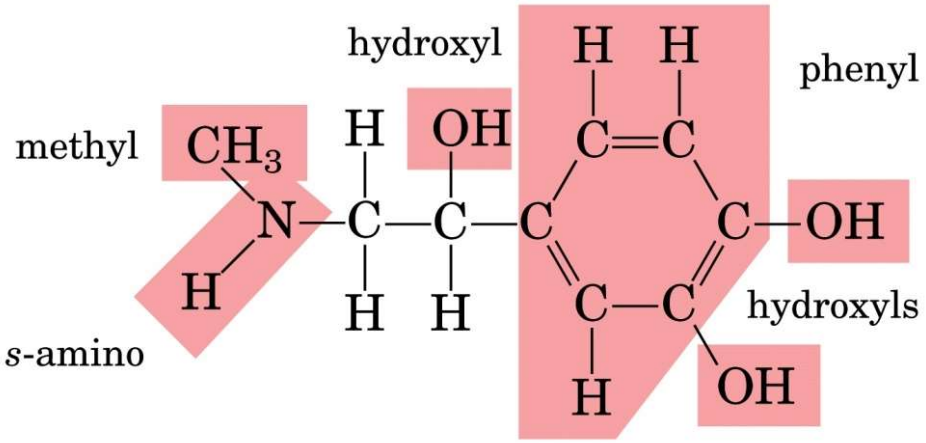


Sulfhydryl

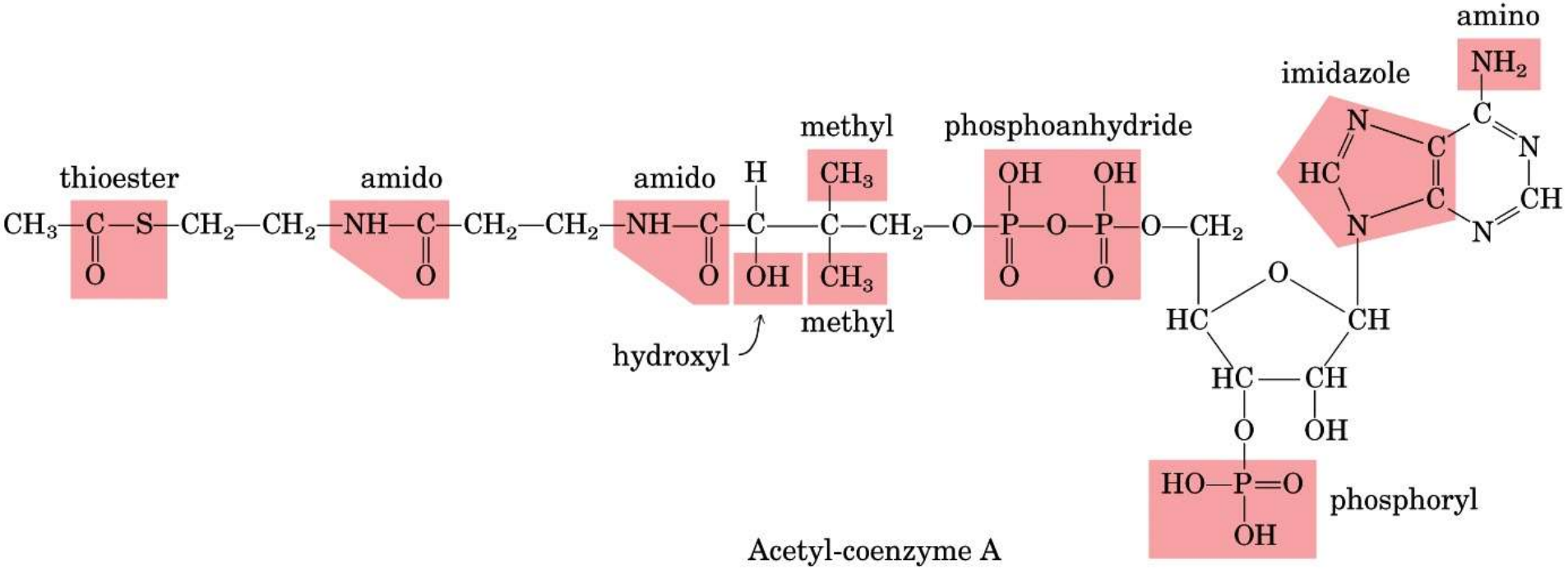




Histidine



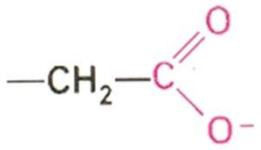
Epinephrine



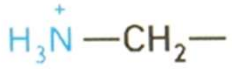
Acetyl-coenzyme A

Interações reversíveis em biomoléculas

1- Ligações eletrostáticas



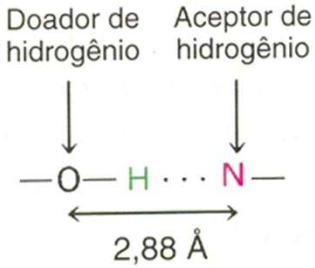
Grupamento com carga negativa de um substrato

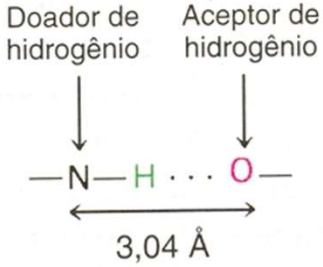


Grupamento com carga positiva de uma enzima

$$F = \frac{q_1 q_2}{r^2 D}$$

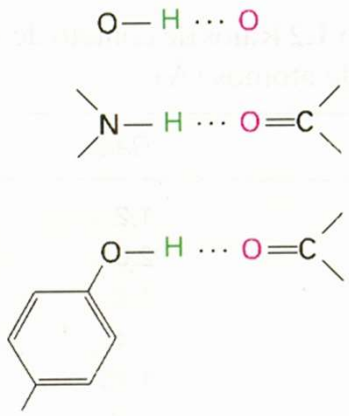
2- Pontes de hidrogênio



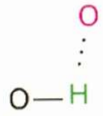


Quadro 1.1 Comprimentos típicos de pontes de hidrogênios

Ligação	*Comprimento* (Å)
O — H .... O	2,70
O — H .... O⁻	2,63
O — H .... N	2,88
N — H .... O	3,04
N⁺ — H .... O	2,93
N — H .... N	3,10

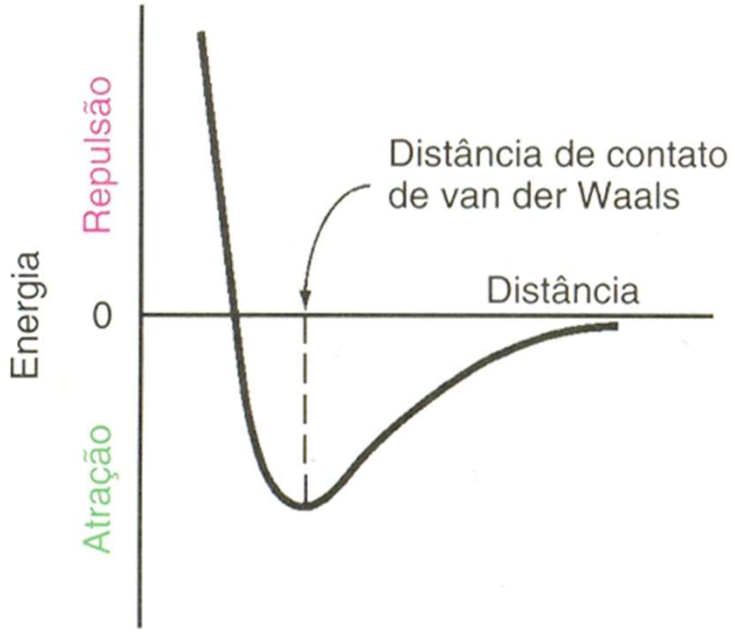


Pontes de hidrogênio fortes



Pontes de hidrogênio fracas

3- Ligações de Van der Waals

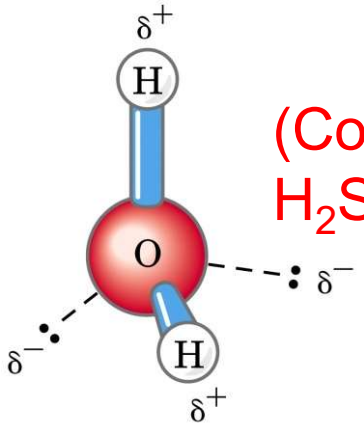


Quadro 1.2 Raios de contato de van der Waals de átomos (Å)

Átomo	*Raio*
H	1,2
C	2,0
N	1,5
O	1,4
S	1,85
P	1,9

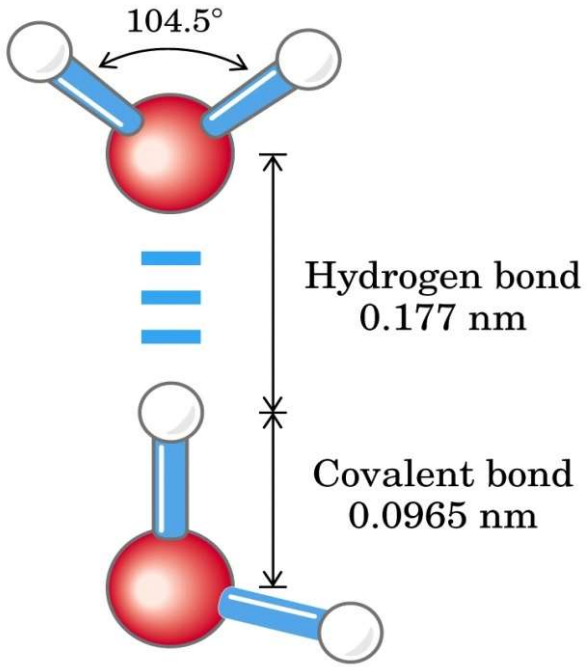
Água

☞ Propriedades



(a)

(Comparação com outros hidretos como H_2S, H_2Se e H_2Te, ponto de ebulição = -100 ºC)



(c)

table 4–1

Melting Point, Boiling Point, and Heat of Vaporization of Some Common Solvents

	Melting point (°C)	Boiling point (°C)	Heat of vaporization (J/g)*
Water	0	100	2,260
Methanol (CH_3OH)	−98	65	1,100
Ethanol (CH_3CH_2OH)	−117	78	854
Propanol ($CH_3CH_2CH_2OH$)	−127	97	687
Butanol ($CH_3(CH_2)_2CH_2OH$)	−90	117	590
Acetone (CH_3COCH_3)	−95	56	523
Hexane ($CH_3(CH_2)_4CH_3$)	−98	69	423
Benzene (C_6H_6)	6	80	394
Butane ($CH_3(CH_2)_2CH_3$)	−135	−0.5	381
Chloroform ($CHCl_3$)	−63	61	247

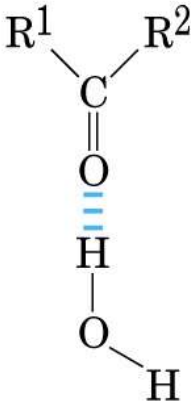
*The heat energy required to convert 1.0 g of a liquid at its boiling point, at atmospheric pressure, into its gaseous state at the same temperature. It is a direct measure of the energy required to overcome attractive forces between molecules in the liquid phase.

Mesmo número de elétrons

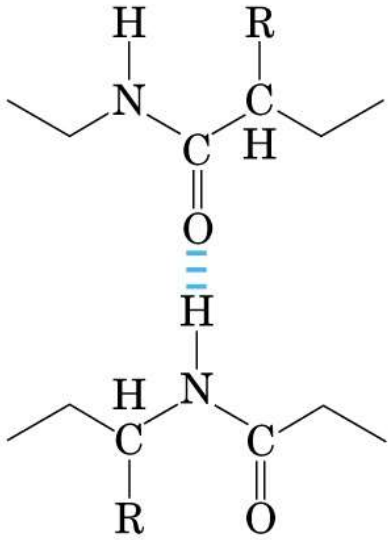
Pontes de hidrogênio de importância biológica

Between the hydroxyl group of an alcohol and water

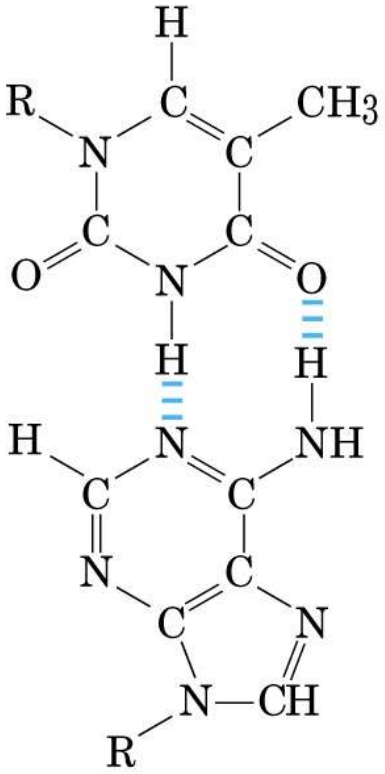
Between the carbonyl group of a ketone and water



Between peptide groups in polypeptides



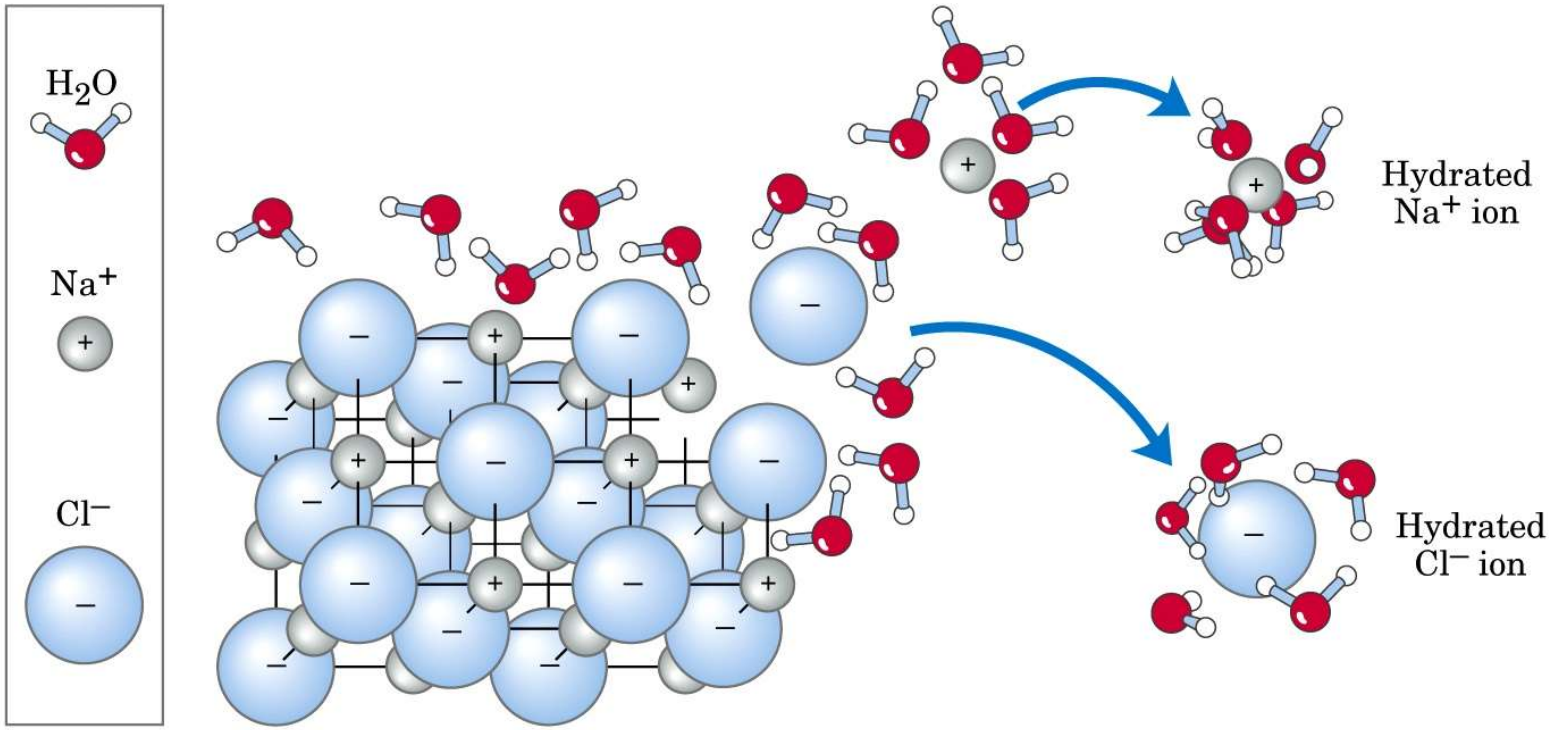
Between complementary bases of DNA



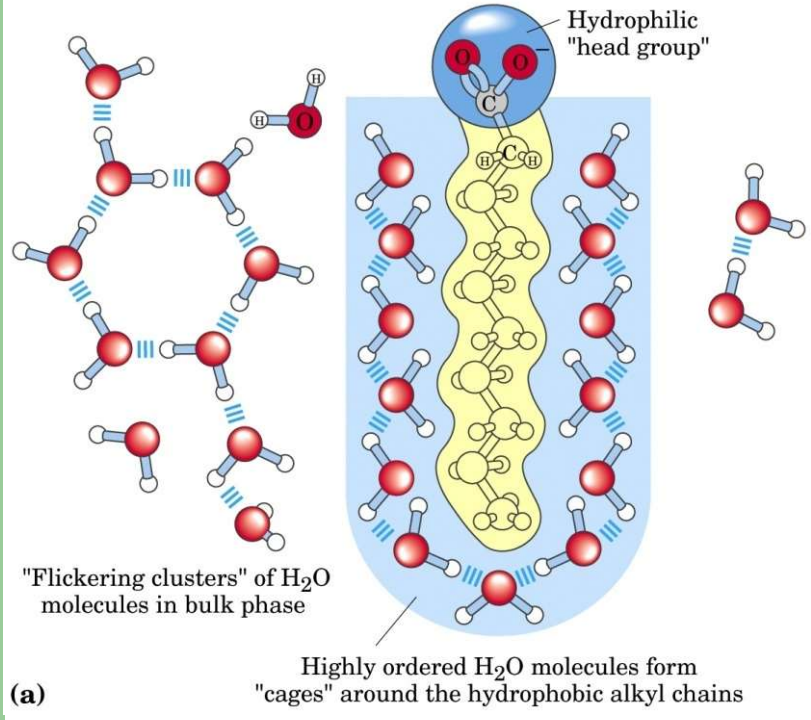
Thymine

Adenine

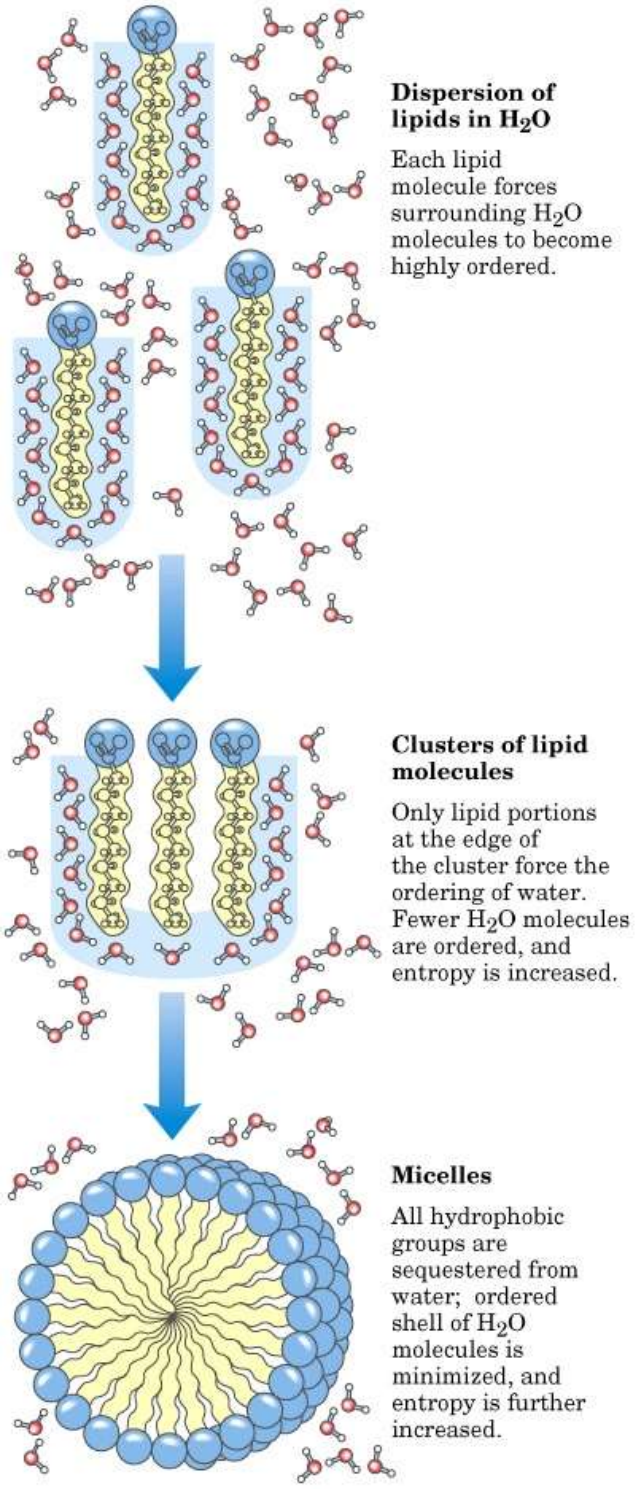
Constante dielétrica



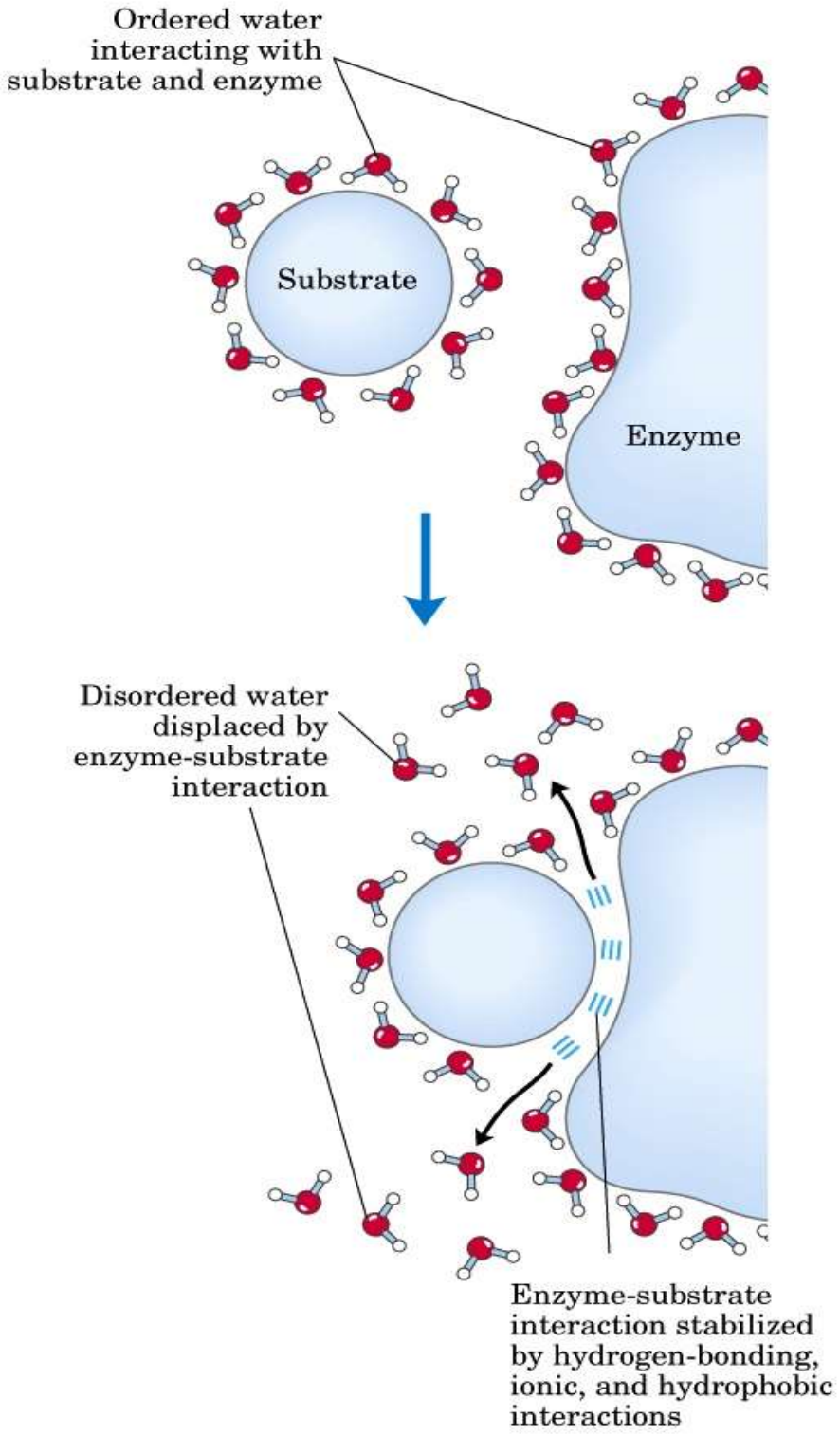
Substância	*Constante dielétrica*
Hexano	1,9
Benzeno	2,3
Éter etílico	4,3
Clorofórmio	5,1
Acetona	21,4
Etanol	24
Metanol	33
Água	80
Ácido cianídrico	116


Hydrophilic
"head group"
"Flickering clusters" of H_2O
molecules in bulk phase
Highly ordered H_2O molecules form
"cages" around the hydrophobic alkyl chains

(a)


Dispersion of lipids in H_2O
Each lipid molecule forces surrounding H_2O molecules to become highly ordered.
Clusters of lipid molecules
Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.
Micelles
All hydrophobic groups are sequestered from water; ordered shell of H_2O molecules is minimized, and entropy is further increased.

(b)


Ordered water interacting with substrate and enzyme
Substrate
Enzyme
Disordered water displaced by enzyme-substrate interaction
Enzyme-substrate interaction stabilized by hydrogen-bonding, ionic, and hydrophobic interactions

Equação de Henderson-Hasselbalch

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

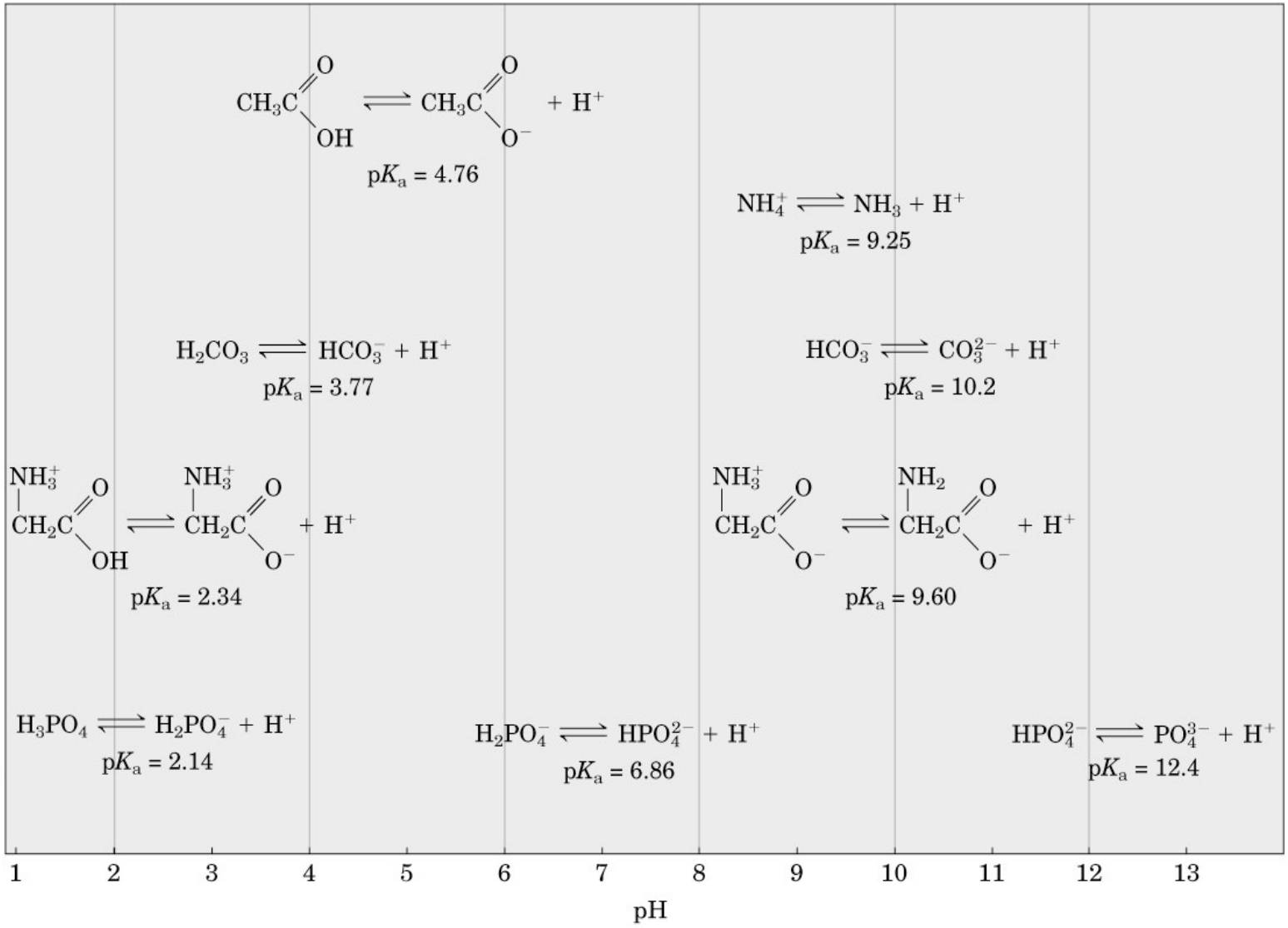
Monoprotic acids
Acetic acid
($K_a = 1.74 \times 10^{-5}$ M)

Ammonium
($K_a = 5.62 \times 10^{-10}$ M)

Diprotic acids
Carbonic acid
($K_a = 1.70 \times 10^{-4}$ M);
Bicarbonate
($K_a = 6.31 \times 10^{-11}$ M)

Glycine, carboxyl
($K_a = 4.57 \times 10^{-3}$ M);
Glycine, amino
($K_a = 2.51 \times 10^{-10}$ M)

Triprotic acids
Phosphoric acid
($K_a = 7.25 \times 10^{-3}$ M);
Dihydrogen phosphate
($K_a = 1.38 \times 10^{-7}$ M);
Monohydrogen phosphate
($K_a = 3.98 \times 10^{-13}$ M)



Bioenergética

Energia livre: função termodinâmica mais útil em Bioquímica

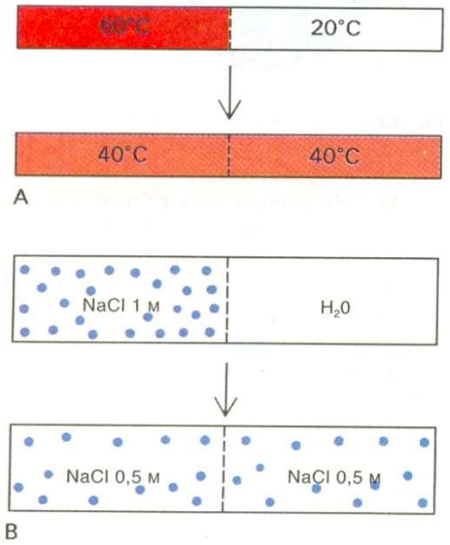
- Sistema: **matéria dentro de uma região definida**
- Circunvizinhança ou ambiente: **matéria do resto do universo**

Primeira lei da termodinâmica: energia total do sistema e da circunvizinhança é constante

$$\Delta E = E_B - E_A = Q - W$$

A primeira lei não pode ser usada para predizer se uma reação ocorre espontaneamente

☞ Entropia: **pode predizer se uma reação bioquímica vai ocorrer espontaneamente (mede o grau de desordem do sistema)**



Segunda lei: a entropia do sistema e da circunvizinhança devem aumentar para um processo espontâneo

$$(\Delta S_{sistema} + \Delta S_{circunvizinhança}) > 0$$

Energia livre (G): combinação da primeira com a segunda

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

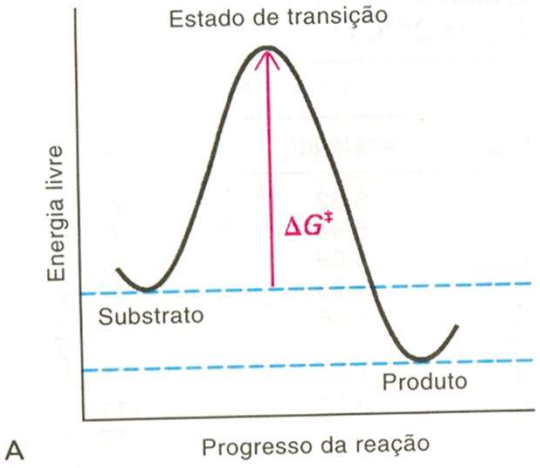
$$\Delta H = \Delta E + P\Delta V$$

$$\Delta G \cong \Delta E - T\Delta S$$

Indica apenas que a reação bioquímica poderá ocorrer espontaneamente, mas não em velocidade perceptível; usar **ΔG‡**

OBS: Não é dependente do caminho das transformações
Ex: glicose

Velocidade de uma reação bioquímica

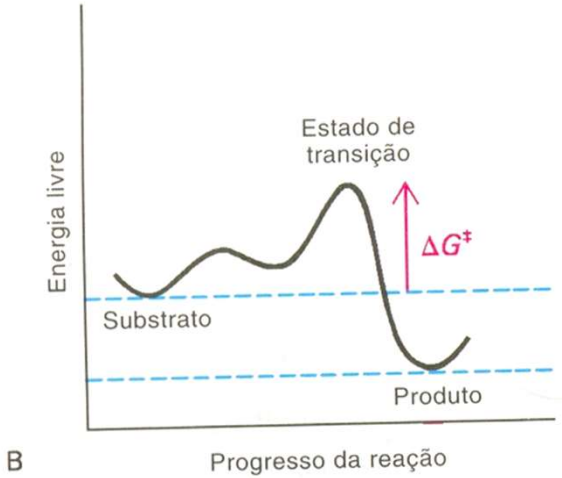


A

$$\Delta G^{\ddagger} = G_{S^{\ddagger}} - G_S$$

$$[S^{\ddagger}] = [S]e^{-\Delta G^{\ddagger}/RT}$$

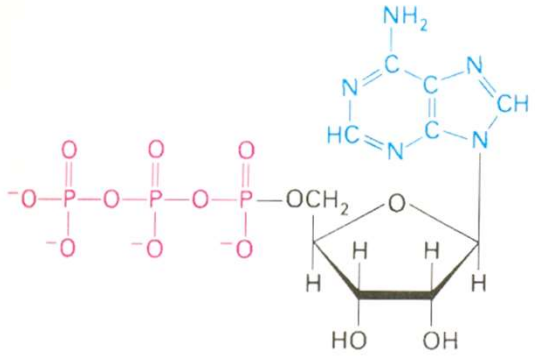
$$V = \nu[S^{\ddagger}] = \frac{kT}{h}[S]e^{-\Delta G^{\ddagger}/RT}$$



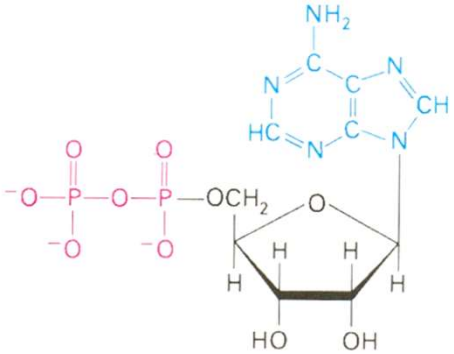
B

Impulsionamento de uma reação bioquímica desfavorável

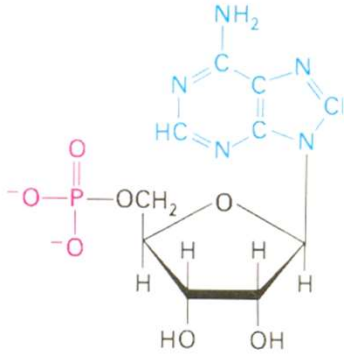
$$A \rightleftharpoons B + C \qquad \Delta G^{\circ\prime} = +5 \text{ kcal/mol}$$
$$B \rightleftharpoons D \qquad \Delta G^{\circ\prime} = -8 \text{ kcal/mol}$$
$$A \rightleftharpoons C + D \qquad \Delta G^{\circ\prime} = -3 \text{ kcal/mol}$$



Adenosina trifosfato (ATP)



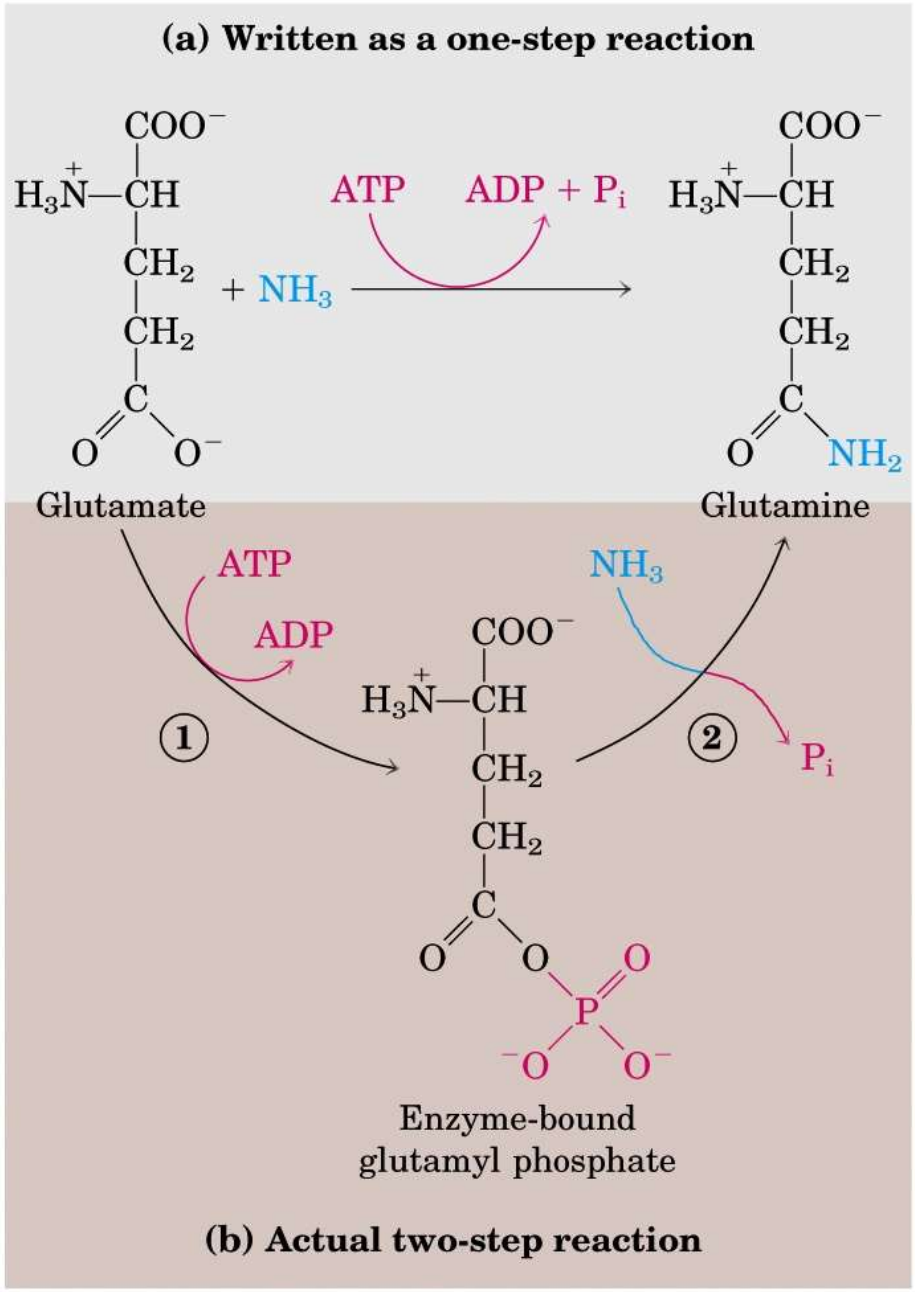
Adenosina difosfato (ADP)



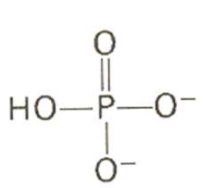
Adenosina monofosfato (AMP)

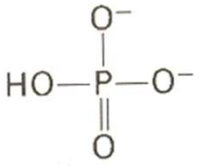
$ATP + H_20 \leftrightarrow ADP + P_i + H^+$ $\qquad \Delta G^{0\prime} = -7{,}3$ kcal/mol

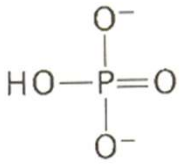
Hidrólise do ATP em duas etapas

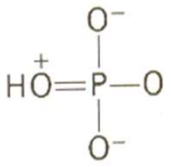


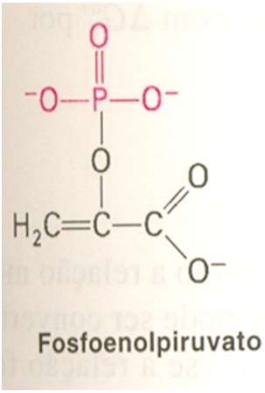
Base estrutural do alto potencial de transferência de fosforilas do ATP



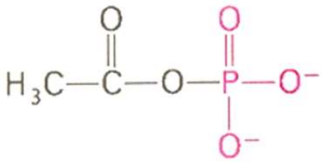




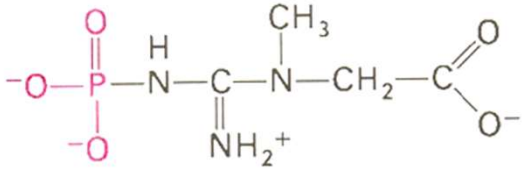




Fosfoenolpiruvato

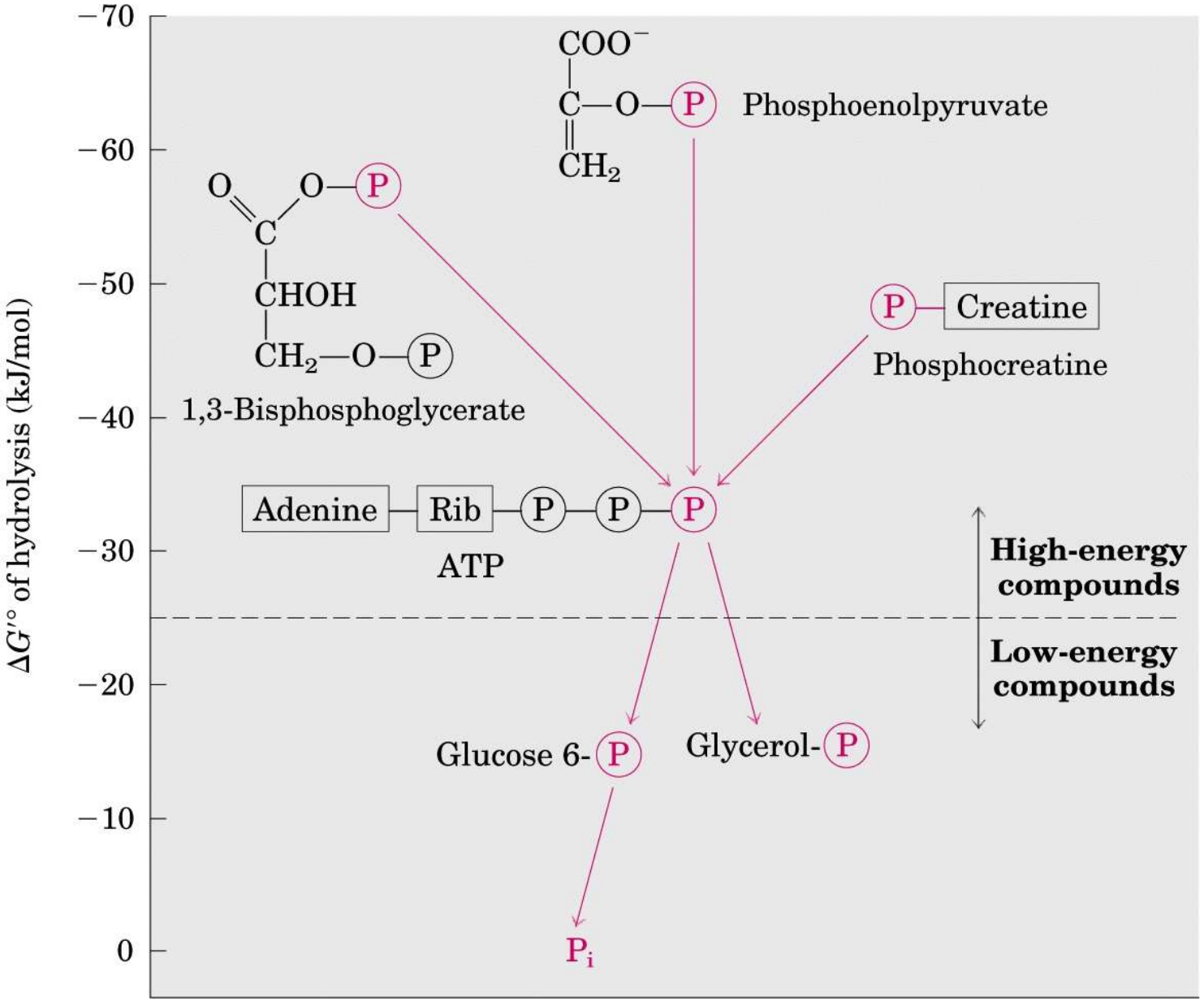


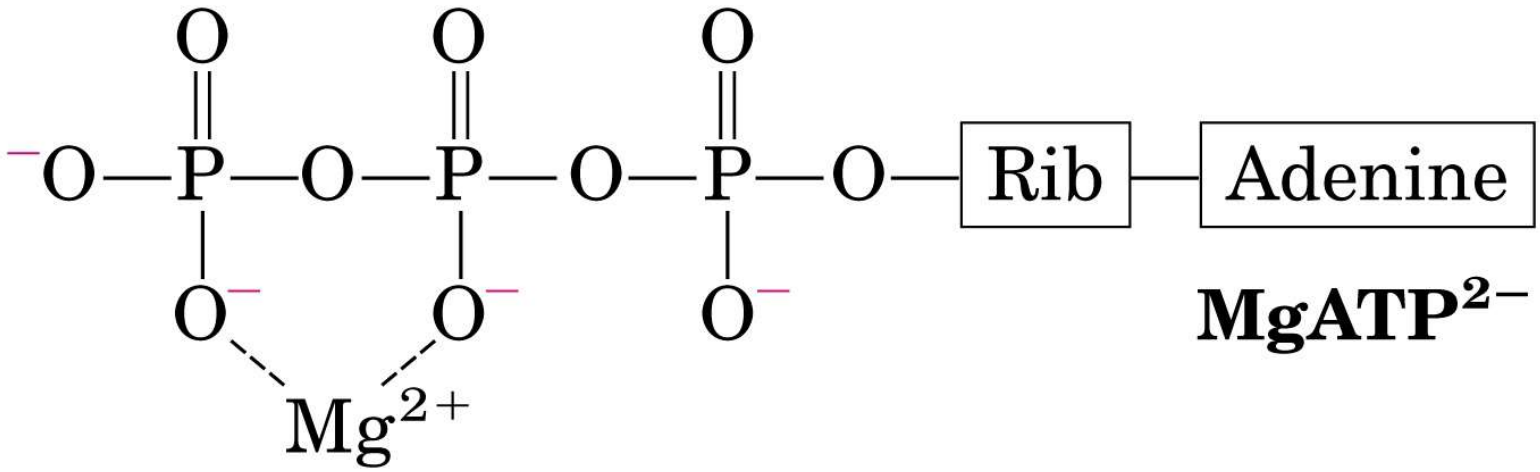
Acetil fosfato



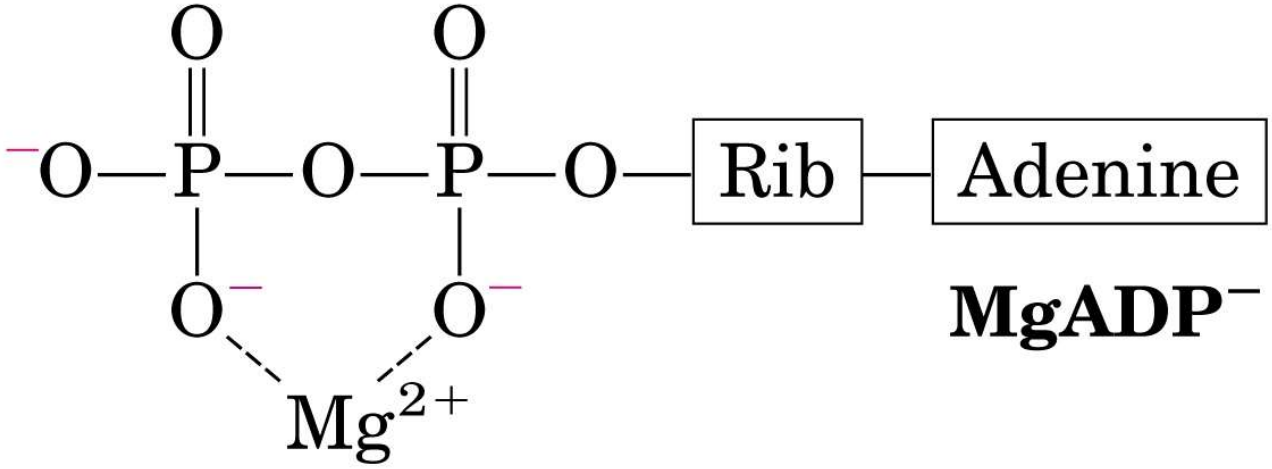
Creatina fosfato

Composto	*ΔG°′ (kcal/mol)*
Fosfoenolpiruvato	−14,8
Carbamil fosfato	−12,3
Acetil fosfato	−10,3
Creatina fosfato	−10,3
Pirofosfato	−8,0
ATP (a ADP)	−7,3
Glicose 1-fosfato	−5,0
Glicose 6-fosfato	−3,3
Glicose 3-fosfato	−2,2


−70
−60
−50
−40
−30
−20
−10
0
ΔG'° of hydrolysis (kJ/mol)
COO⁻
C—O—P
CH₂
Phosphoenolpyruvate
O O—P
C
CHOH
CH₂—O—P
1,3-Bisphosphoglycerate
P—Creatine
Phosphocreatine
Adenine
Rib
P
P
P
ATP
High-energy compounds
Low-energy compounds
Glucose 6-P
Glycerol-P
Pi

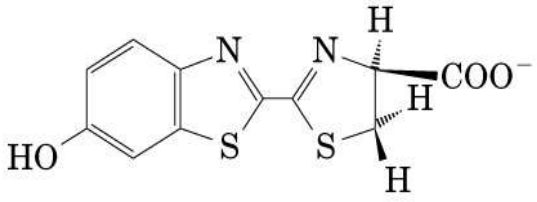


MgATP^{2-}

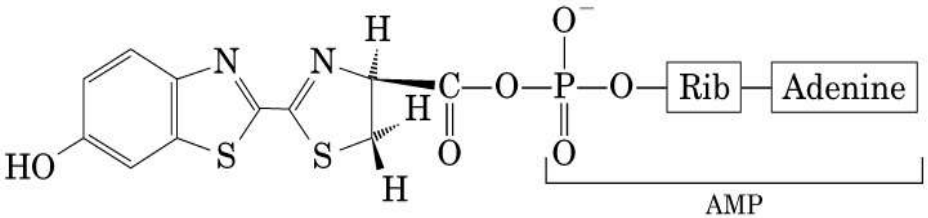


MgADP^{-}

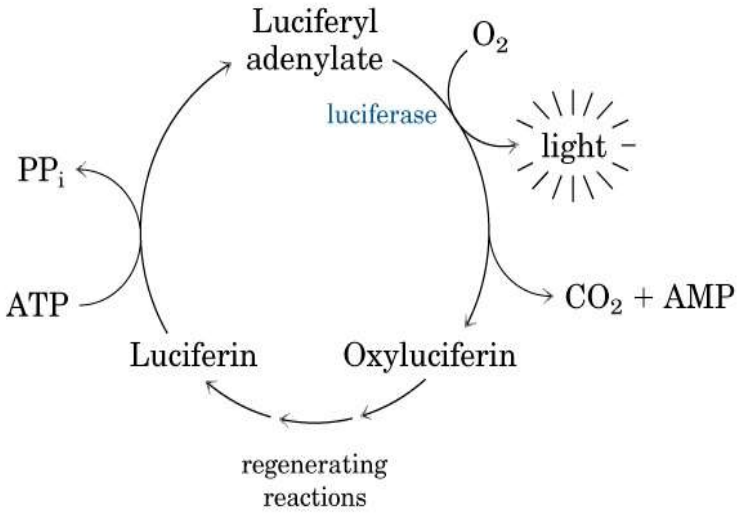
Emissão de energia luminosa por vaga-lumes



Firefly luciferin

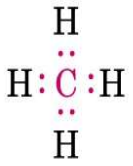
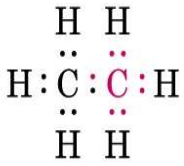
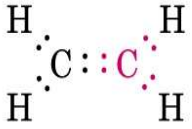
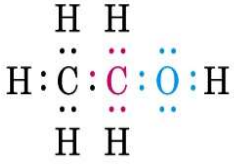
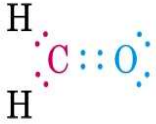
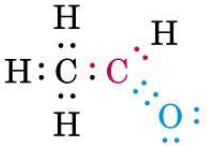
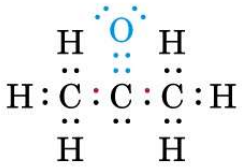
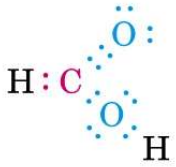
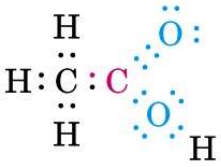


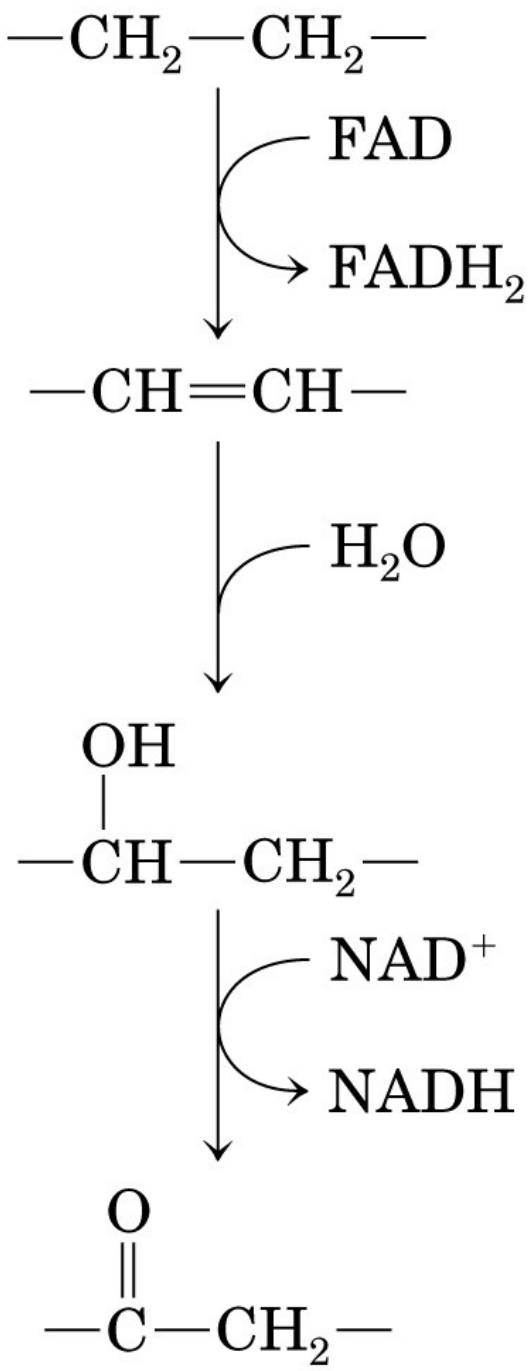
Luciferyl adenylate



Oxidações biológicas

Reações de desidrogenação

Methane		8
Ethane (alkane)		7
Ethene (alkene)		6
Ethanol (alcohol)		5
Acetylene (alkyne)		5
Formaldehyde		4
Acetaldehyde (aldehyde)		3
Acetone (ketone)		2
Formic acid (carboxylic acid)		2
Carbon monoxide		2
Acetic acid (carboxylic acid)		1
Carbon dioxide		0


—CH2—CH2—
FAD
FADH2
—CH=CH—
H2O
OH
—CH—CH2—
NAD+
NADH
O
—C—CH2—

NADH e NADPH: coenzimas que atuam com desidrogenases no transporte de elétrons solúveis

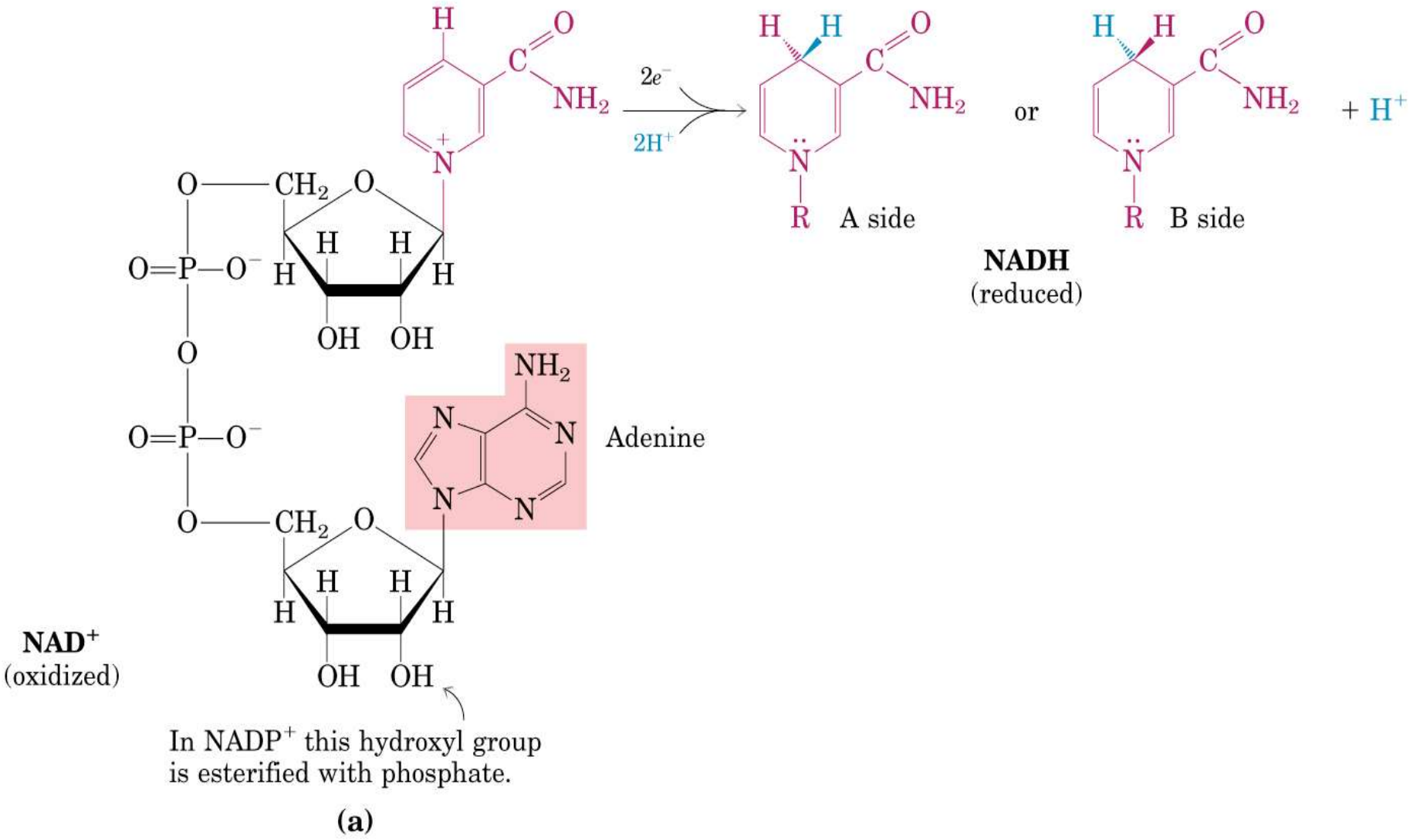
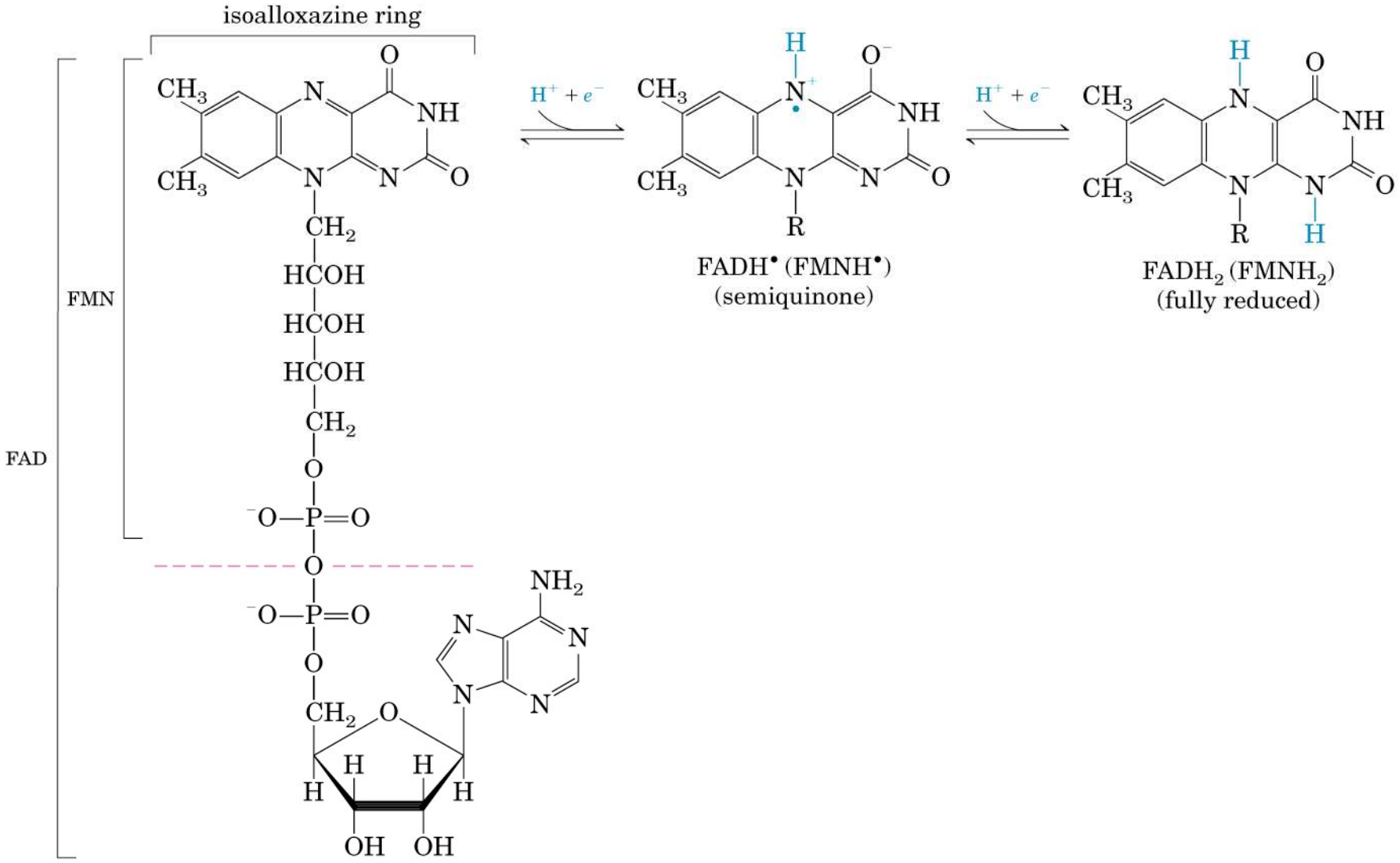


table 14–8

Stereospecificity of Dehydrogenases That Employ NAD^+ or $NADP^+$ as Coenzymes

Enzyme	Coenzyme	Stereochemical specificity for nicotinamide ring (A or B)
Isocitrate dehydrogenase	NAD^+	A
α-Ketoglutarate dehydrogenase	NAD^+	B
Glucose 6-phosphate dehydrogenase	$NADP^+$	B
Malate dehydrogenase	NAD^+	A
Glutamate dehydrogenase	NAD^+ or $NADP^+$	B
Glyceraldehyde 3-phosphate dehydrogenase	NAD^+	B
Lactate dehydrogenase	NAD^+	A
Alcohol dehydrogenase	NAD^+	A



Flavin adenine dinucleotide (FAD) and
flavin mononucleotide (FMN)

table 14–9

Some Enzymes (Flavoproteins) That Employ Flavin Nucleotide Coenzymes

Enzyme	Flavin nucleotide
Fatty acyl–CoA dehydrogenase	FAD
Dihydrolipoyl dehydrogenase	FAD
Succinate dehydrogenase	FAD
Glycerol 3-phosphate dehydrogenase	FAD
Thioredoxin reductase	FAD
NADH dehydrogenase (Complex I)	FMN
Glycolate dehydrogenase	FMN