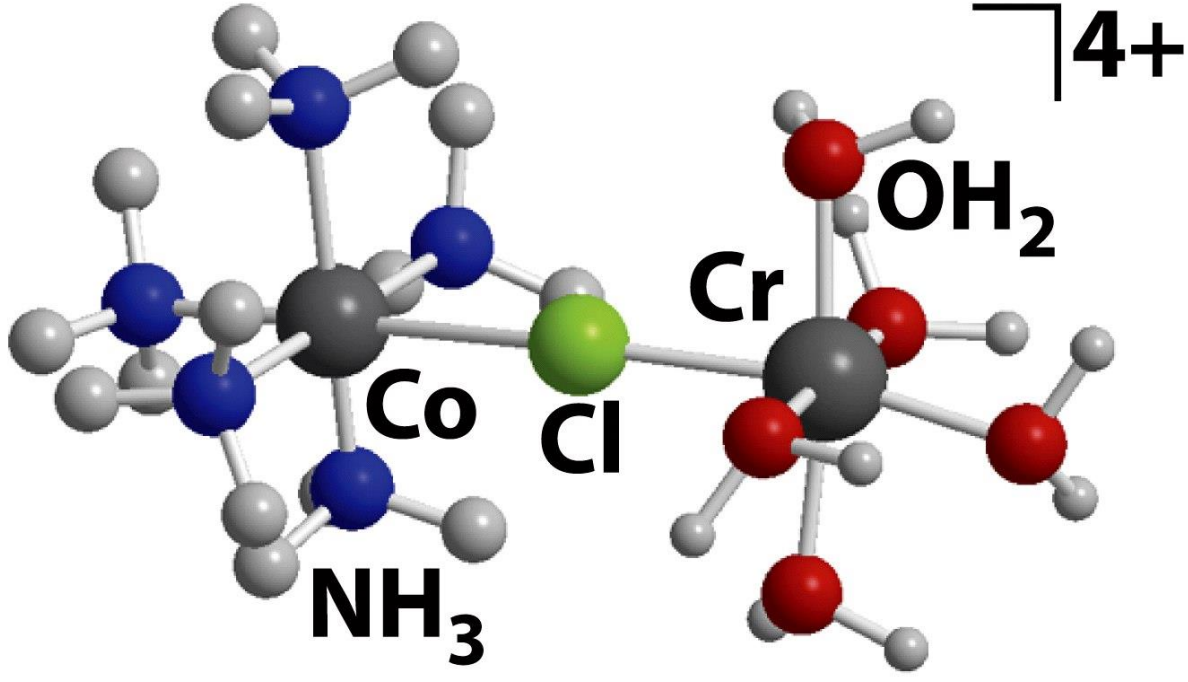
Processi redox a sfera interna

(*Henry Taube, Nobel 1983*)

$$[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} + 5H_3O^+ \rightarrow$$

$$[Co(OH_2)_6]^{2+} + [Cr(OH_2)_5Cl]^{2+} + 5NH_4^+$$



Processo redox senza trasferimento del legante a ponte

$$[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \rightarrow$$

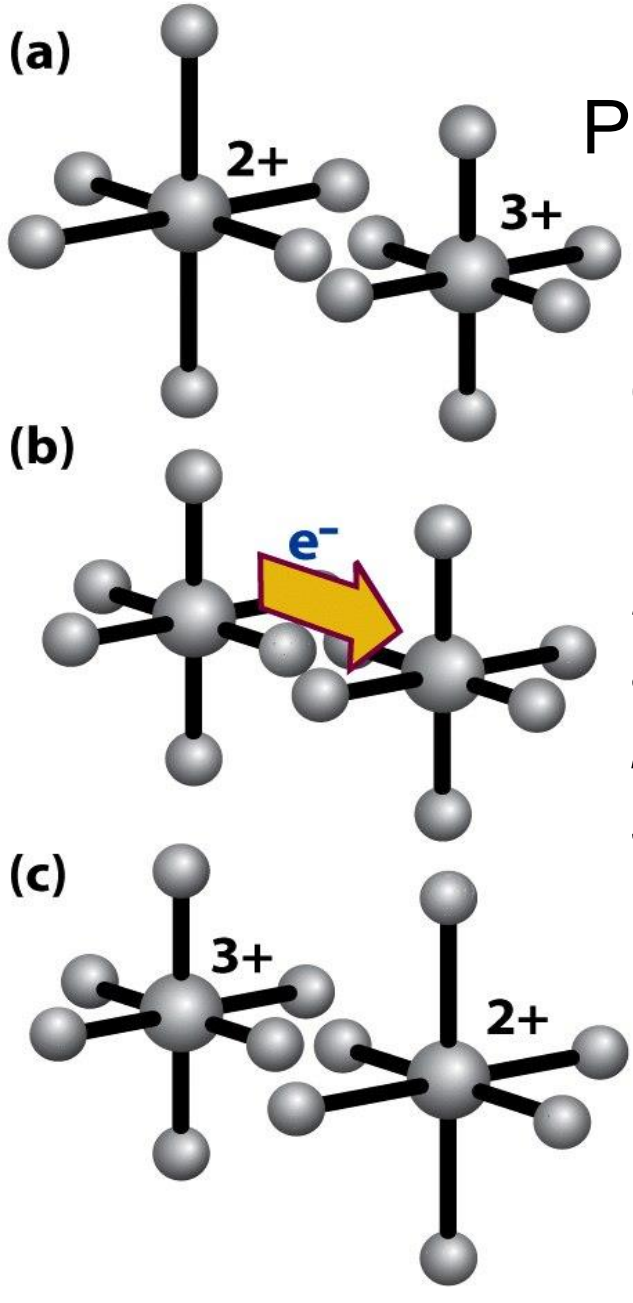
$$[Fe(CN)_5(\mu\text{-}CN)Co(CN)_5]^{6-} \rightarrow$$

$$[Fe(CN)_6]^{4-} + [Co(CN)_5(OH_2)]^{2-}$$

Processi redox a sfera esterna

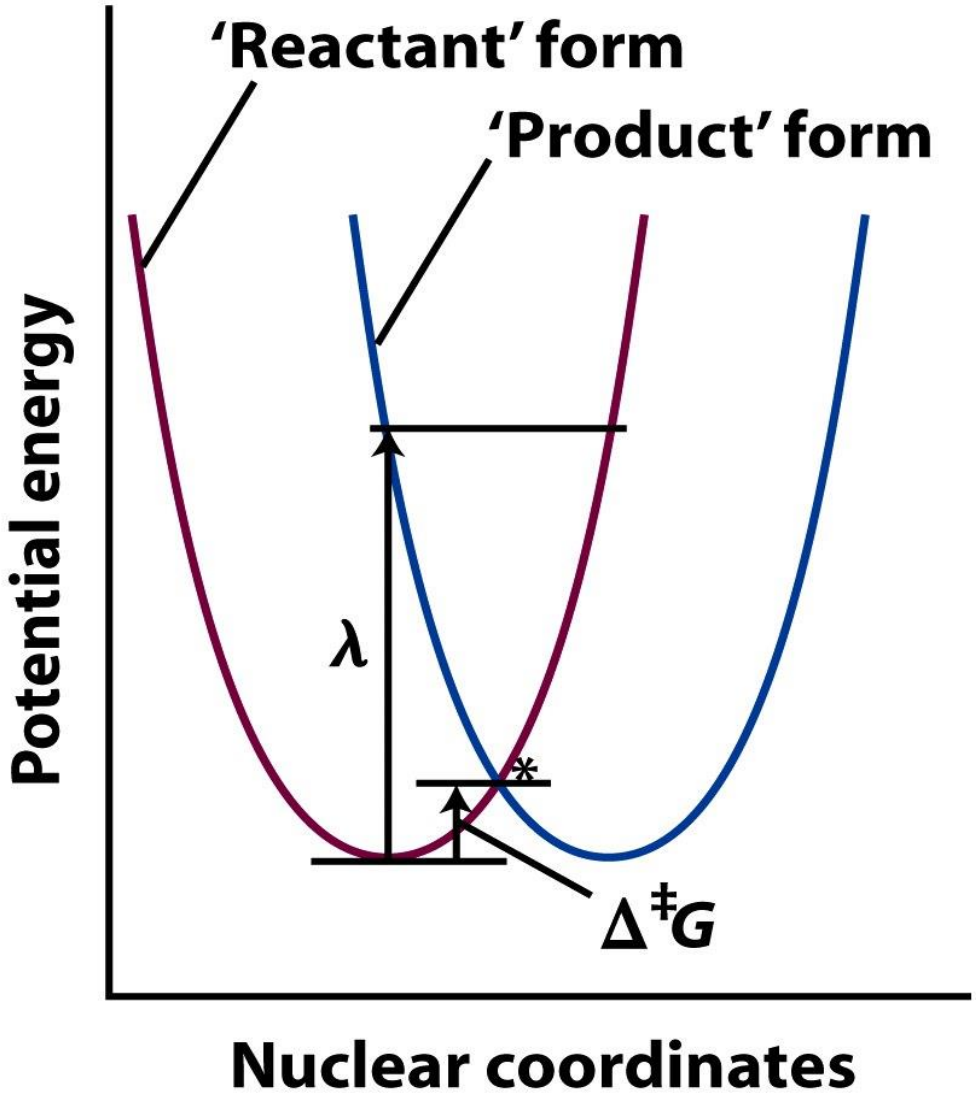
	Reaction	k / dm^3 mol^{-1} s^{-1}
No net chemical reaction (self-exchange)	$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \rightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$>10^6$
	$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \rightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$>10^6$
	$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \rightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
	$[Fe(OH_2)_6]^{2+} + [Fe(OH_2)_6]^{3+} \rightarrow [Fe(OH_2)_6]^{3+} + [Fe(OH_2)_6]^{2+}$	3
	$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \rightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
	$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
Net chemical reaction	$[Os(bpy)_3]^{2+} + [Mo(CN)_8]^{3-} \rightarrow [Os(bpy)_3]^{3+} + [Mo(CN)_8]^{4-}$	2×10^9
	$[Fe(CN)_6]^{4-} + [Fe(phen)_3]^{3+} \rightarrow [Fe(CN)_6]^{3-} + [Fe(phen)_3]^{2+}$	10^8
	$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$	4×10^5

Principio di Frank – Condon



Complesso di incontro

La transizione elettronica può avvenire <u>solo quando</u> le lunghezze di legame M-L siano le stesse sia per M(II) che per M(III)


'Reactant' form
'Product' form
Potential energy
λ
*
$\Delta^{\ddagger}G$
Nuclear coordinates

Velocità di trasferimento elettronico

$k_{ET} = \nu_N \kappa_e e^{-\Delta G^{\neq}/RT}$ Equazione di Marcus

(*Rudolph Marcus, Nobel 1992*)

ν_N = fattore di frequenza nucleare[a]

κ_e = fattore elettronico (0 ÷ 1)[b]

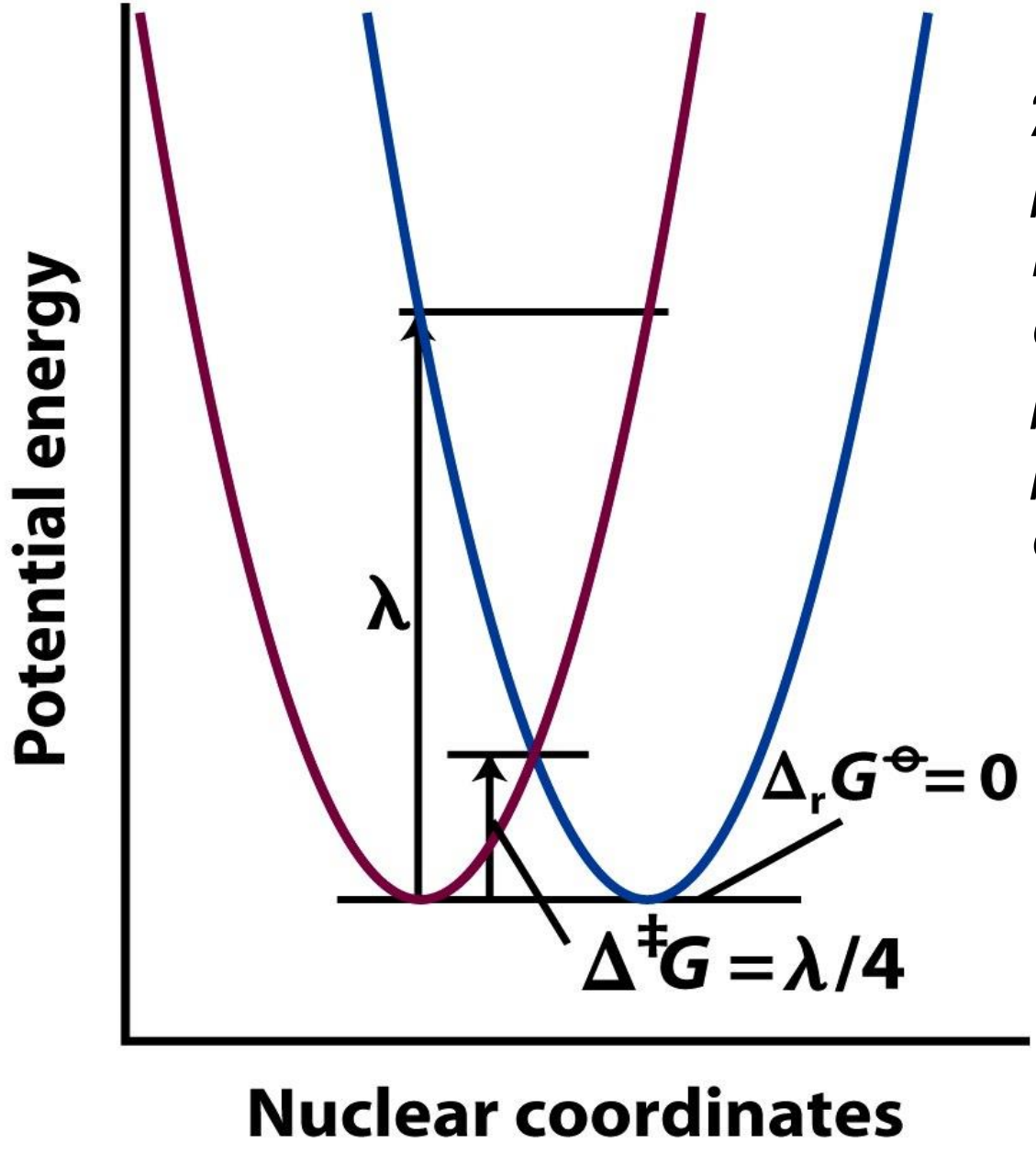
$$\Delta G^{\neq} = \frac{\lambda}{4} \times (1 + \frac{\Delta G^{\circ}}{\lambda})^2$$

λ = **energia di riorganizzazione**

$$\Delta G^{\neq} = \frac{\lambda}{4}$$ per self-exchange

[a] *frequenza alla quale le due specie, dopo aver formato il complesso di incontro in soluzione, raggiungono lo stato di transizione.*

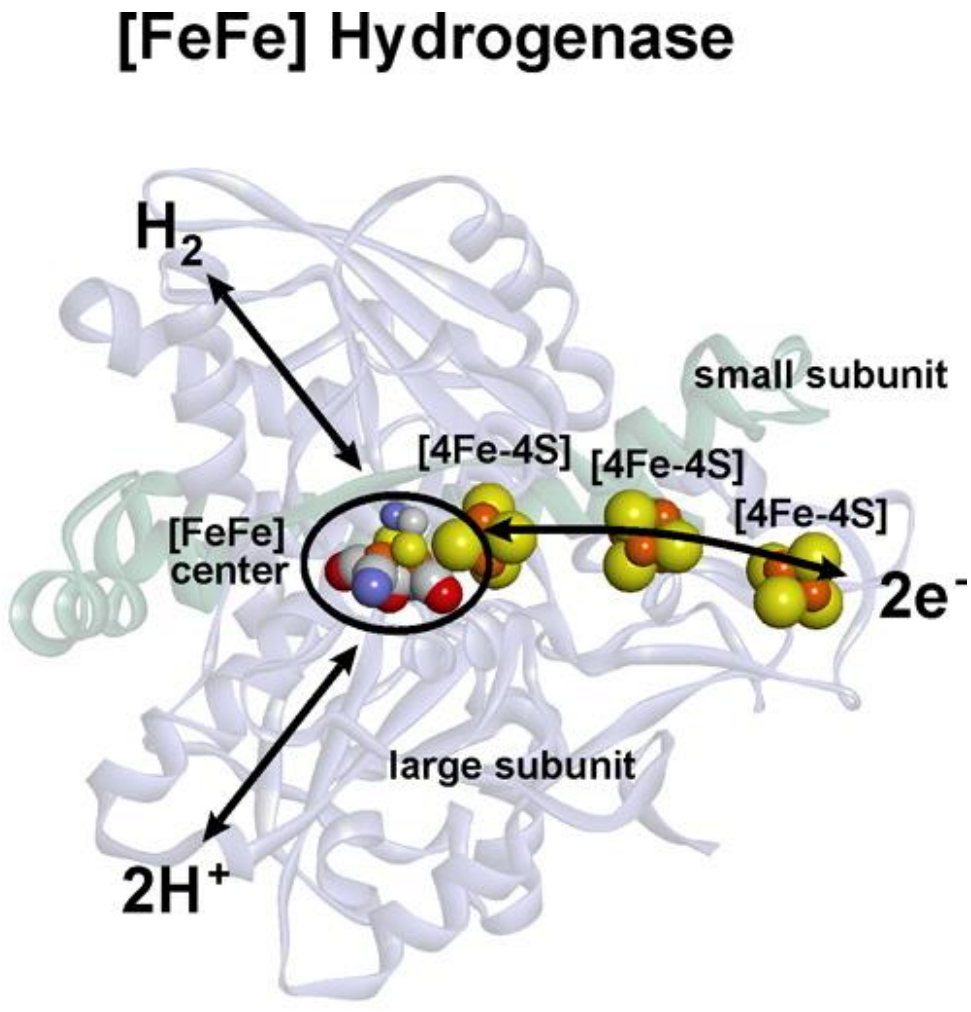
[b] *probabilità, in una scala da 0 a 1, che avvenga il trasferimento di un elettrone quando sia stato raggiunto lo stato di transizione. Dipende dalla sovrapposizione degli orbitali di donatore e accettore.*



λ è l'energia necessaria per muovere i nuclei del reagente nelle posizioni che essi assumono nel prodotto immediatamente prima del trasferimento elettronico

tipicamente $\lambda > 1$ eV (vs. ca. 0.25 V nei metallo enzimi per electron transfer)

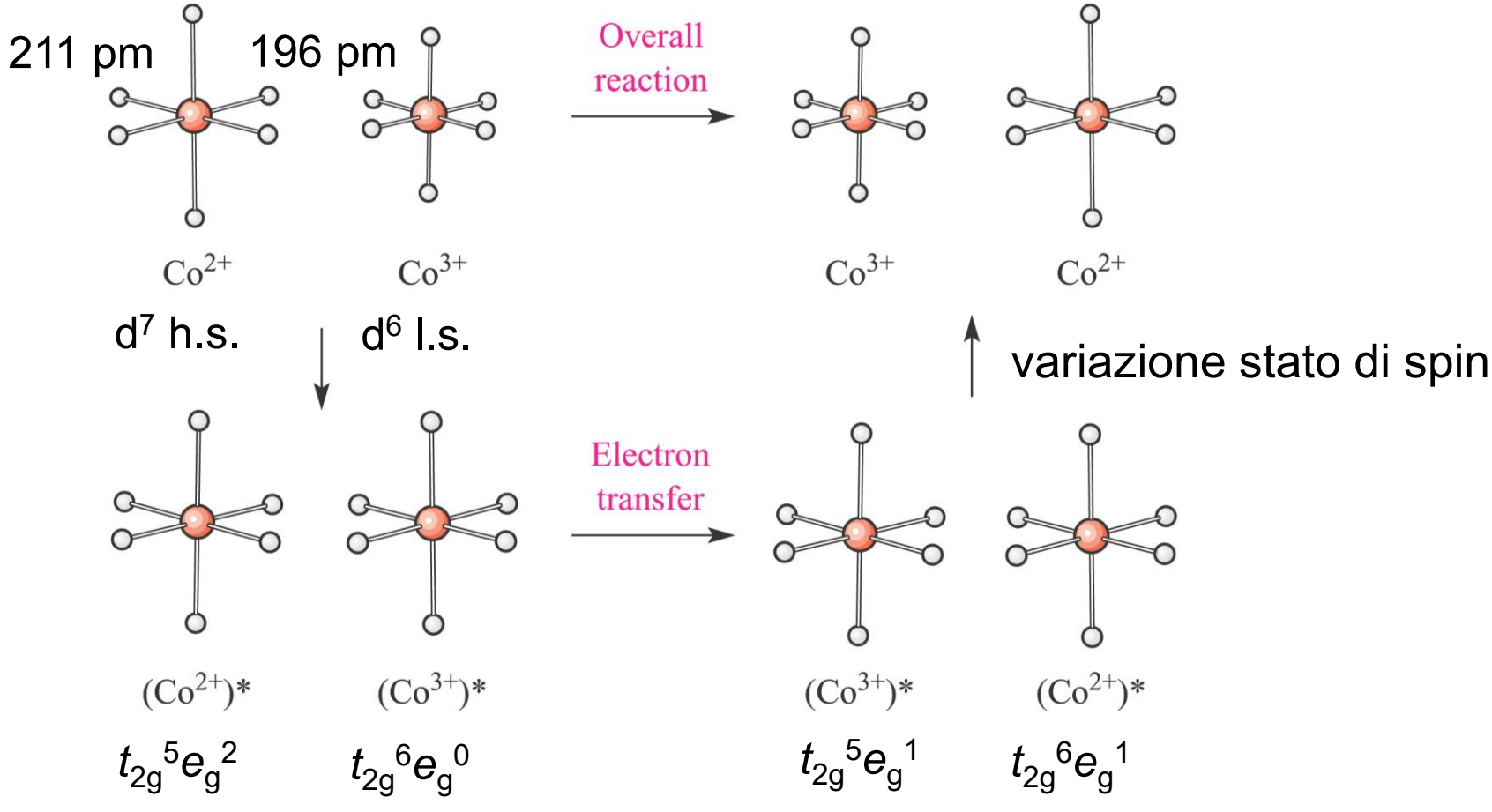
Reazioni redox a sfera esterna in ambito biologico



Processi redox a sfera esterna

	Reaction	k / dm^3 mol^{-1} s^{-1}
No net chemical reaction (self-exchange)	$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \rightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$>10^6$
	$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \rightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$>10^6$
	$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \rightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
	$[Fe(OH_2)_6]^{2+} + [Fe(OH_2)_6]^{3+} \rightarrow [Fe(OH_2)_6]^{3+} + [Fe(OH_2)_6]^{2+}$	3
	$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \rightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
	$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
Net chemical reaction	$[Os(bpy)_3]^{2+} + [Mo(CN)_8]^{3-} \rightarrow [Os(bpy)_3]^{3+} + [Mo(CN)_8]^{4-}$	2×10^9
	$[Fe(CN)_6]^{4-} + [Fe(phen)_3]^{3+} \rightarrow [Fe(CN)_6]^{3-} + [Fe(phen)_3]^{2+}$	10^8
	$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$	4×10^5

Elevata energia di riorganizzazione λ in $[Co(NH_3)_6]^{3+/2+}$



stati vibrazionali eccitati

Reazioni non *self exchange*

la costante di velocità per il trasferimento elettronico aumenta esponenzialmente quanto più il $\Delta G°$ diventa negativo, cioè quanto più la reazione diventa termodinamicamente favorita

$$\Delta G^{\neq} = \frac{\lambda}{4} \times (1 + \frac{\Delta G°}{\lambda})^2$$

se $|\Delta G°| \ll |\lambda|$

$$\Delta G^{\#} \approx 1/4 \times (\lambda + 2\Delta G°)$$

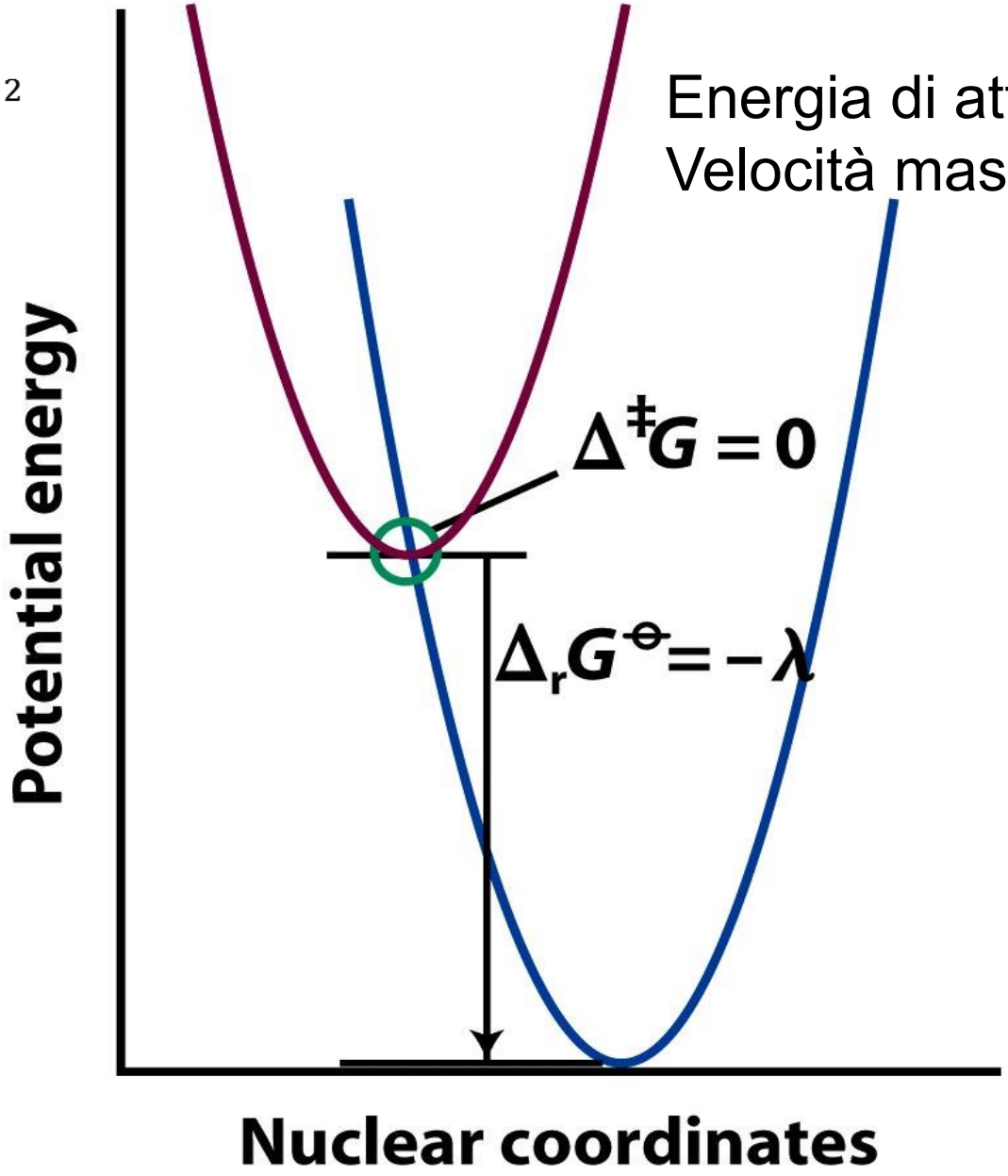
$$k_{ET} \approx \nu_N \kappa_e e^{-(\lambda + 2\Delta G°)/4RT}$$

$$\lambda + 2\Delta G° > 0$$

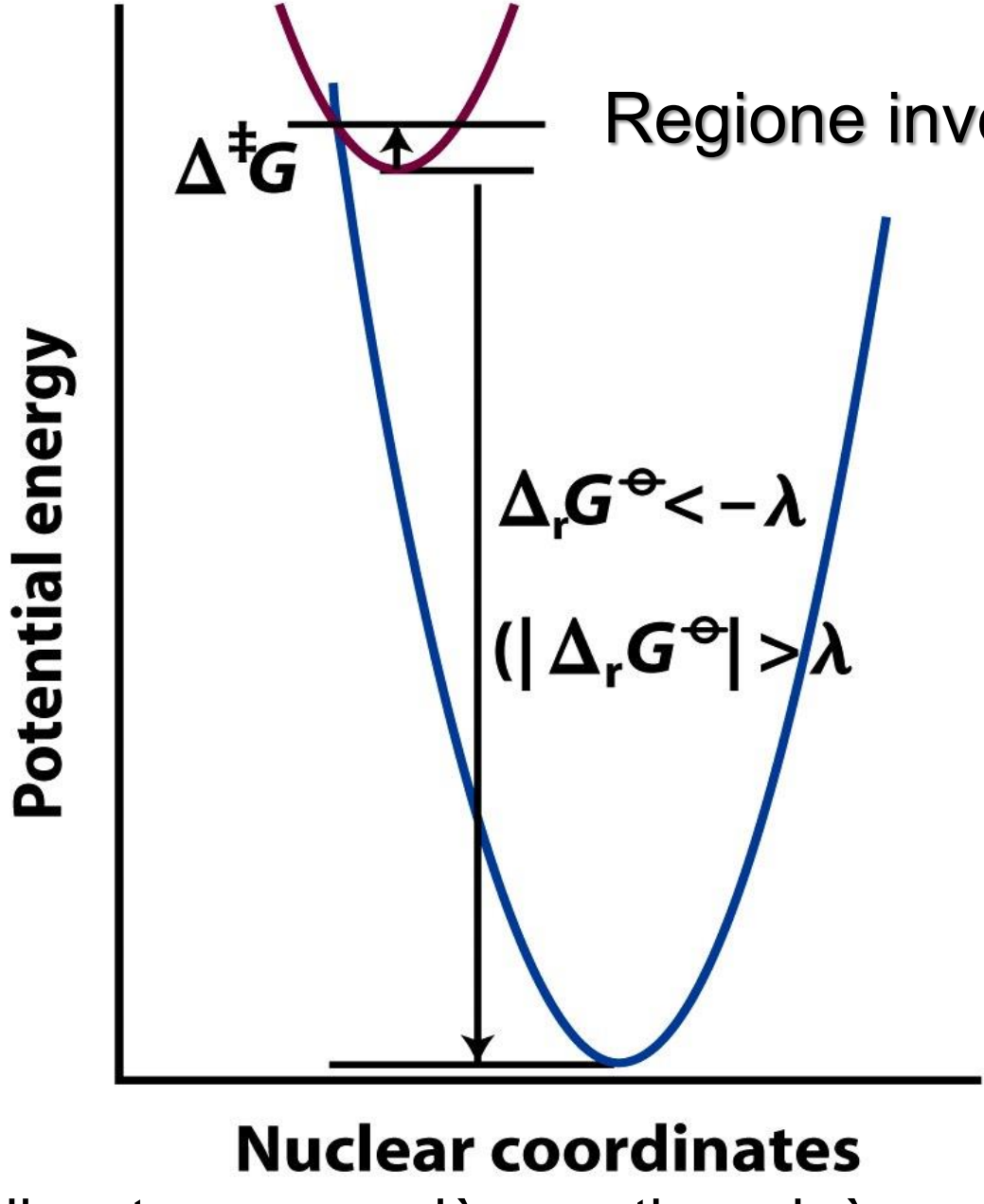
tanto più negativo è $\Delta G°$ e tanto più piccolo è $\Delta G^{\#}$

$$\Delta G^{\neq} = \frac{\lambda}{4} \times (1 + \frac{\Delta G^{\circ}}{\lambda})^2$$

Energia di attivazione nulla
Velocità massima

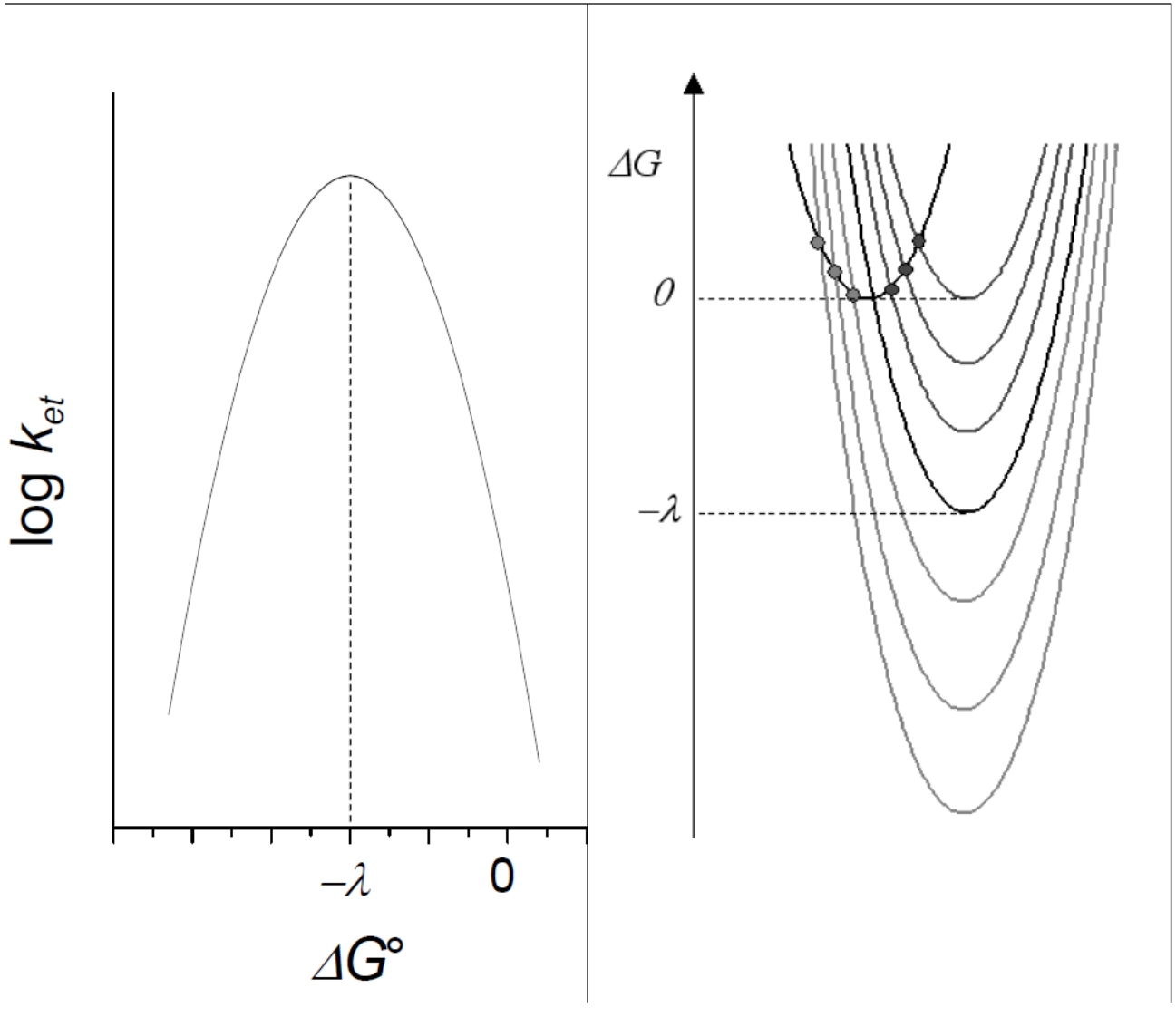


quando $\Delta G° = -\lambda$ l'energia di attivazione è nulla la costante cinetica raggiunge un massimo

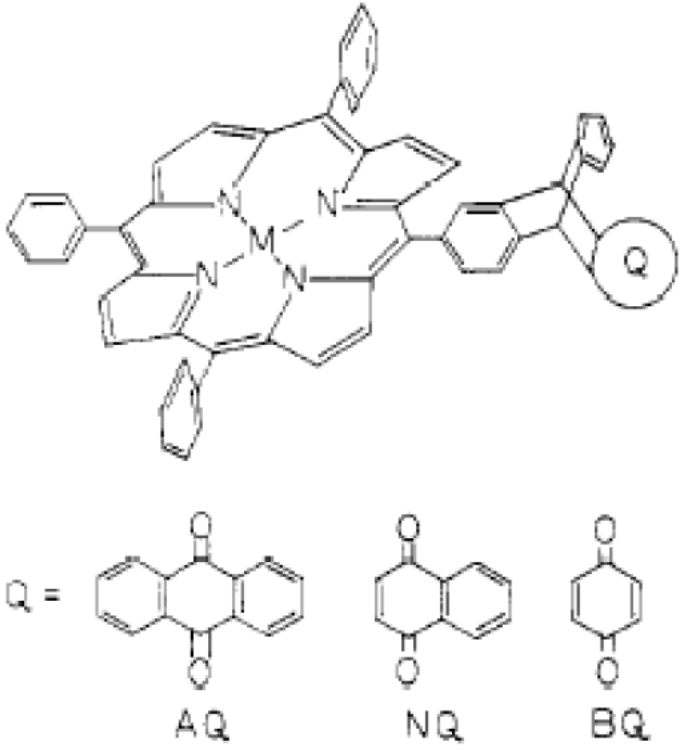


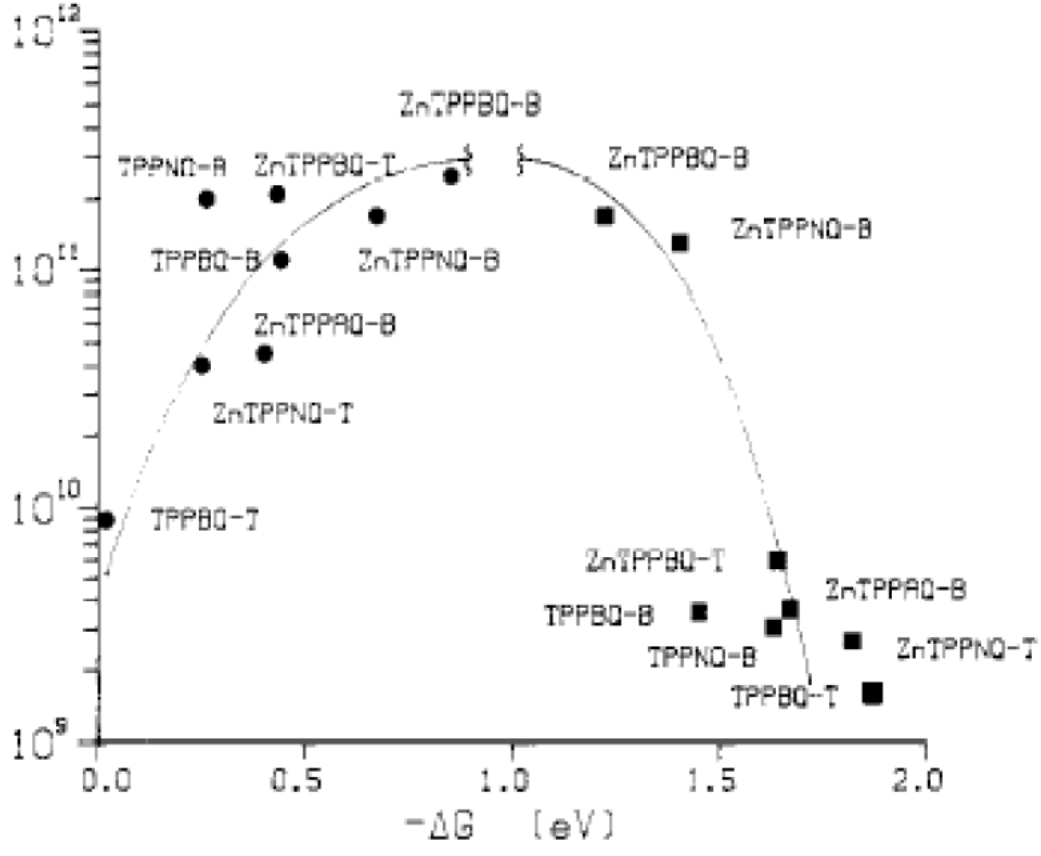
Quando poi $\Delta G°$ diventa ancora più negativo, cioè quando $|\Delta G°| > |\lambda|$, l'energia di attivazione aumenta e quindi **la velocità diminuisce**

Andamento della velocità di trasferimento elettronico in funzione del $\Delta G°$ secondo l'equazione di Marcus

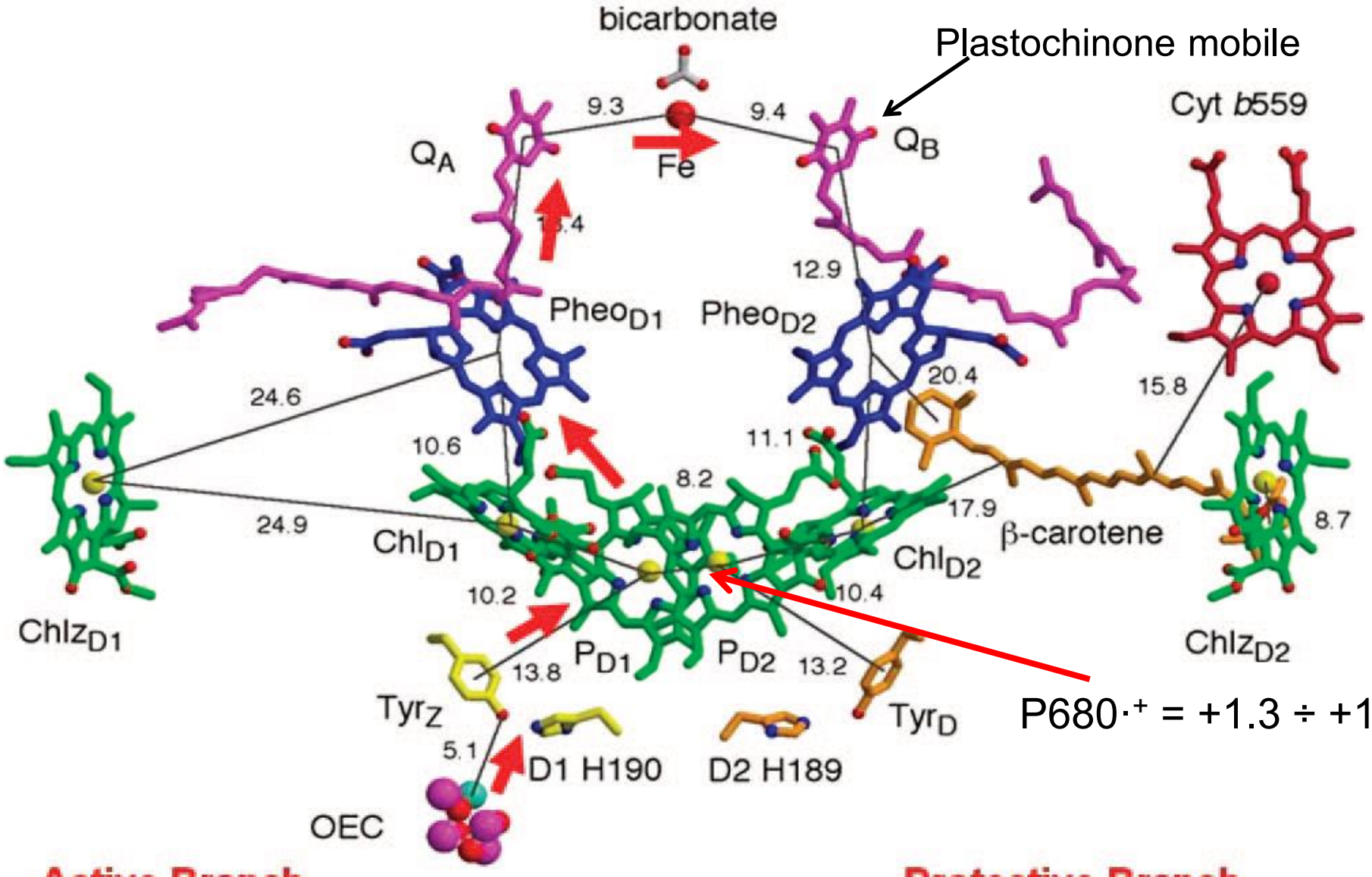


Dipendenza della velocità di ET in una diade covalente in funzione della esoergonicità



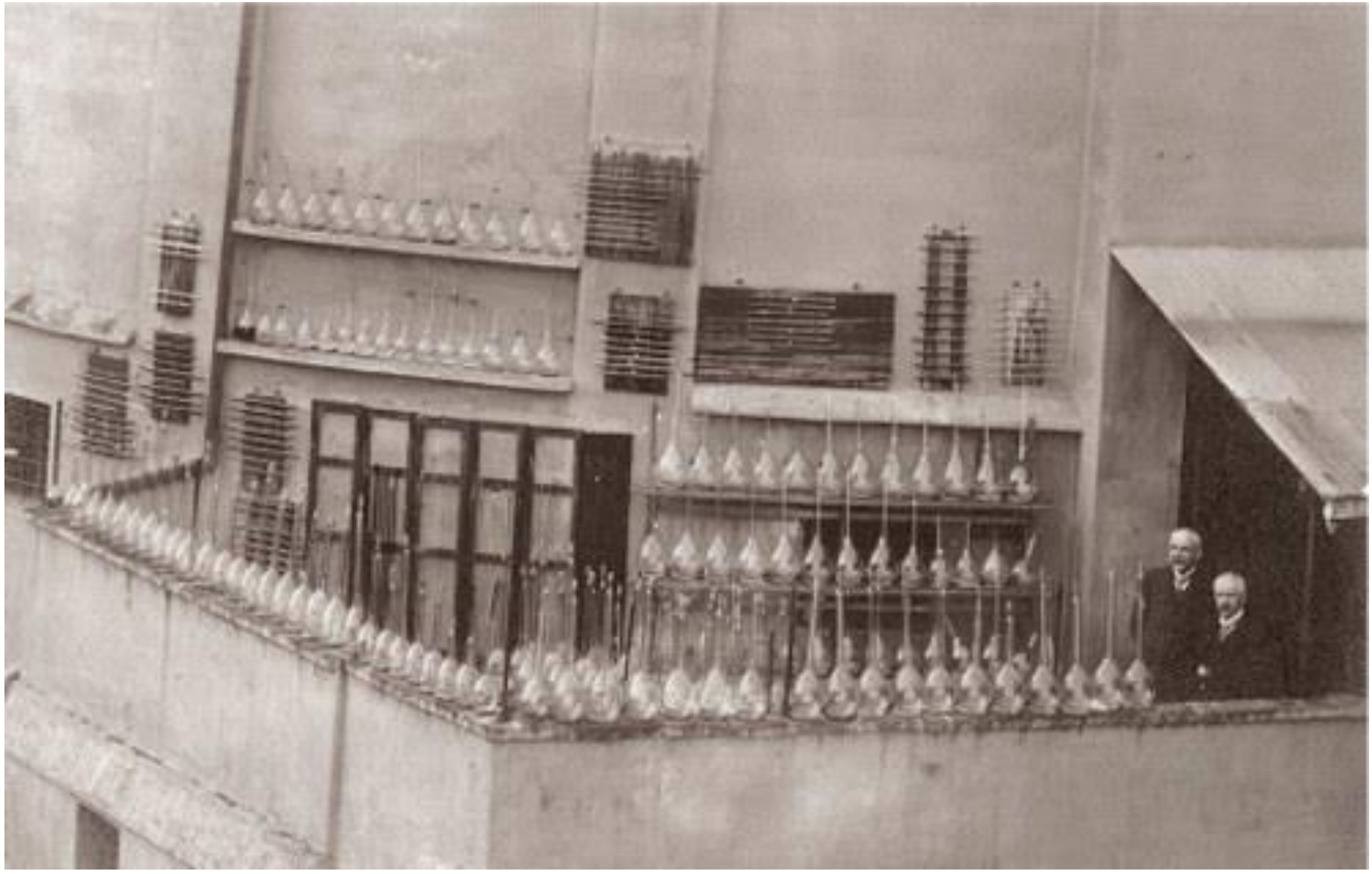


Electron transport cofactors

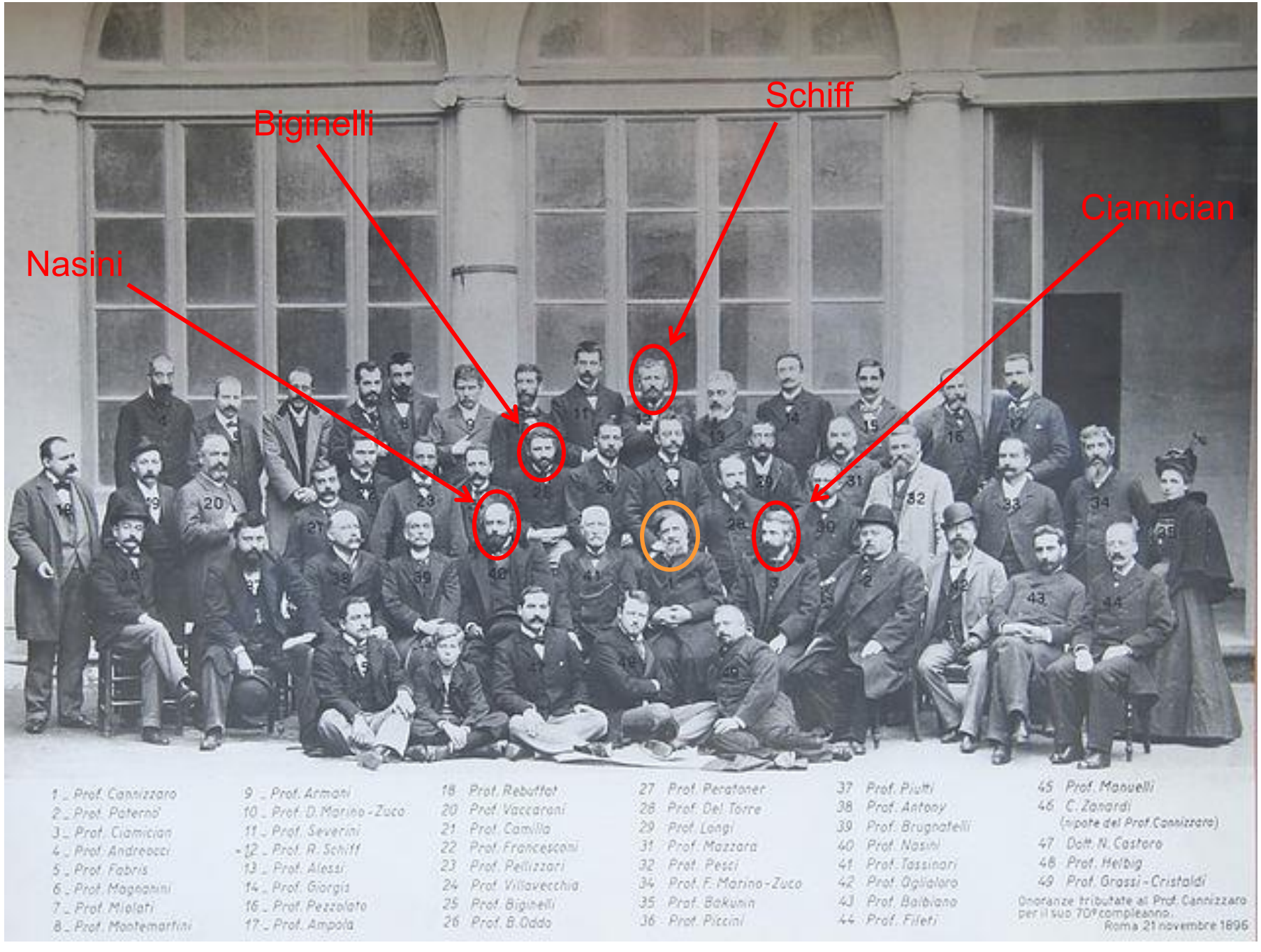


Giacomo Luigi Ciamician

Trieste, 1857 – Bologna, 1922



Celebrazione dei 70 anni di Cannizzaro (1896)



SCIENCE

FRIDAY, SEPTEMBER 27, 1912

CONTENTS

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of SCIENCE, Garrison-on-Hudson, N. Y.

THE PHOTOCHEMISTRY OF THE FUTURE[1]

MODERN civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

THE PHOTOCHEMISTRY OF THE FUTURE (1912)

GIACOMO CIAMICIAN (1857-1922)
(Translation supplied by the author)

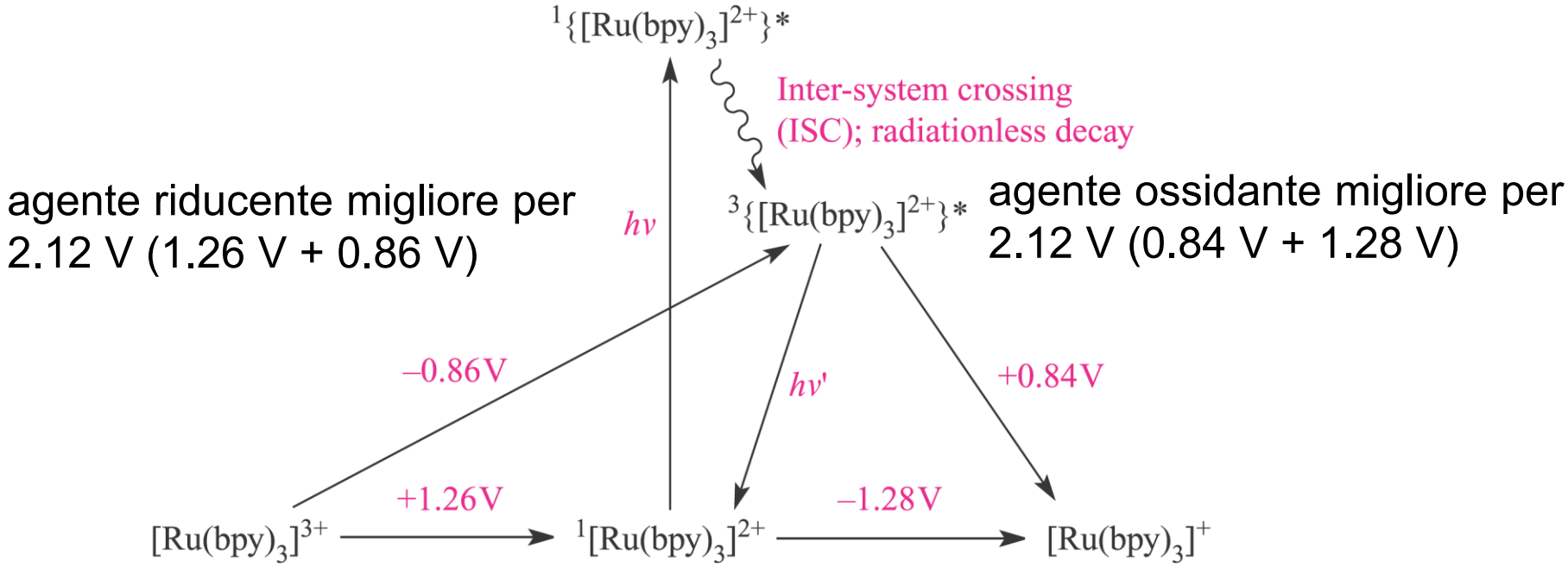
Modern civilization is the daughter of coal for this offers to mankind the solar energy in its most concentrated form: that is in a form in which it has been accumulated in a long series of centuries.

And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.
The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?

Giacomo Ciamician, uno scienziato oltre i confini del suo tempo

Prof. Vincenzo Balzani

https://www.youtube.com/watch?v=RzGFCrq39v0


$^1\{[Ru(bpy)_3]^{2+}\}^*$
Inter-system crossing
(ISC); radiationless decay
agente riducente migliore per
2.12 V (1.26 V + 0.86 V)
$h\nu$
$^3\{[Ru(bpy)_3]^{2+}\}^*$
agente ossidante migliore per
2.12 V (0.84 V + 1.28 V)
–0.86 V
$h\nu'$
+0.84 V
+1.26 V
–1.28 V
$[Ru(bpy)_3]^{3+}$
$^1[Ru(bpy)_3]^{2+}$
$[Ru(bpy)_3]^{+}$