



























Ground state
(gas phase)
$$D + A \longrightarrow D^{\bullet +} + A^{\bullet -}$$

 $\Delta G_{et} = (IP)D - (EA)A$ Excited state
(gas phase)* $D + A \longrightarrow D^{\bullet +} + A^{\bullet -}$
* $\Delta G = (IP)_D - (EA)A - E^*D$ Excited state
In solution $\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_{exc}(A) + \Delta E_{Coulombic}$ $\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_{exc}(A) + \Delta E_{Coulombic}$ Rehm-Weller Equation

Gas Phase to Solution

The free energy of electron transfer processes in solution can be estimated by two different approaches:

> The value of ΔG for the gas phase reaction is calculated using IP and EA and then corrected to take into account the solvation energies for all the participants (i.e. , *D, *A, D* and A⁻ in the electron transfer reaction.

> The electrochemical potentials for the oxidations E° (D+/D) and reductions E° (A/A-) in solution are measured and then employed to calculate ΔG directly for the solution electron transfer.

> The key electrochemical parameters are more commonly available or can be determined using standard electrochemical techniques, such as cyclic voltammetry; as a result, the second approach is most commonly used.





- a good Donor has a low oxidation potential
- a good Acceptor has a LOW reduction potential
- in the ground state $\Delta G_{redox} > 0$



Be careful about the sign

It is very important to note that by convention in electrochemistry, both E° (D/D++) and E° (A/A+-) are expressed as <u>reductions</u> (D++/D and A/A+-). Both reactions are expressed as $A + e \rightarrow A^{-}$ and D++ $e \rightarrow D$. Because of this convention, one must pay careful attention to the signs of E° (D++/D) and E° (A/A+-) when computing the overall value of ΔG .

Be careful about the reference electrode

Another important point in using electrochemical data is that one must employ the standard electrode to which the values of E° (D+/D) and E° (A/A-) refer. Both the standard <u>hydrogen electrode and the standard calomel electrode and silver electrode</u> are commonly used as standards. So care must be taken to know which is being used and not to mix data from the two standards unless appropriate corrections are made.













		CIECI	roc	inen	ιισαι	Redox Potentials
No.	Compound	E _M (X ⁺ /X) (V vs. SCE) MeCN	Ref	Endons. E _M (X/X ⁻) (V vs. SCE) DMF	Ref	
1	Acenaphthene	+1.21	[6301]	-2.67	[7001]	
2	Acetylene, diphenyl-	-		-2.11	[7701]	THE PARTY AND ADDRESS OF
3	Anthracene	+1.09	[6301]	-1.95	[7701]	HANDBOOK OF
4	Anthracene, 9,10-bis(phenylethynyl)-	+1.165	[6701]	-1.29	[6701]	PHOTOCHEMISTR
5	Anthracene, 9,10-dimethyl-	+0.95	[6401]	-		
6	Anthracene, 9,10-diphenyl-	+1.22	[7701]	-1.94	[7701]	THIRD EDITION
7	Anthracene, 9-methyl-	+0.96	[6301]	-1.97 ^a	[6201]	CONTRACTOR OF THE OWNER
8	Anthracene, 9-phenyl-	-		-1.86	[7001]	and the second
9	Azulene	+0.71	[6301]	-1.65ª	[6201]	A DESCRIPTION OF THE OWNER OF THE
10	Benz[a]antracene	+1.18	[6301]	-		
Tab	le 7b-7 Halfwave Redox Potentials	s of Nitriles.	<i>E</i> _% (A/A ⁻) <i>E₁₀</i>	(A/A ⁻)	Marco Montalti Alberto Credi Luca Prodi M. Teresa Gandolfi
190.	Compound	(V)	DMF ^a	uoue) (Vi	IeCN	AND THE CARGEST SCHOOLS OF JUSC ANE DE UND THREFTED DAT
1	Anthracene, 9-cyano-		-	-	1.58 ^b	Dator & H
2	Anthracene, 9,10-dicyano-		-	_	0.98 ^b	
3	Benzene, 1-cyano-3,5-dinitro-		-0.96		-	
4	Benzene, 1-cyano-4-nitro-		-1.25		-	
5	Benzene, 1.2-dicyano-		-2.12		_	



















- R. A. Marcus, J. Chem. Phys., 24, 966, 1956.
- R. A. Marcus and N. Sutin, *Biochemica et Biophysica Acta*, *811*, 265, **1985**.
- R. A. Marcus, Electron transfer Reactions in Chemistry: Theory and Experiment, (Nobel Lecture) Angew. Chem. Int. Ed., 32, 1111, **1993**.

R. A. Marcus

- Rates are expected:
- \diamond to be slow for weakly exothermic reactions,
- to increase to a maximum for moderately exothermic reactions, and then
- \diamond to decrease with increasing exothermicity for highly exothermic et reactions.









Predictions

The consequences of expressing the free energy of activation in terms of the driving force and λ

 $\Delta \mathbf{G}^{\#} = (\Delta \mathbf{G}^{\circ} + \lambda)^2 / 4\lambda$

1. For an iso-energetic self-exchange reaction one obtains:

For $\Delta G^\circ = 0$ one obtains $\Delta G^\# = \lambda/4$

For $\Delta G^\circ = -\lambda$ one obtains $\Delta G^\# = 0$

2. At this stage the reaction becomes barrierless and proceeds at the maximum rate allowed by the pre-exponential factor.







The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.



The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.





























Back electron transfer & Generation of excited states
$D^{+\bullet} + A^{-\bullet} \xrightarrow{k_{bet}} D^{*} + A$
When back electron transfer to the ground state
$D^{\bullet+} + A^{\bullet-} \rightarrow D + A$ ΔG^{0}_{et} large
is in the Marcus inverted region and is therefore inhibited;
the formation of the excited products
$D^{\bullet+} + A^{\bullet-} \rightarrow D^{\bullet+} A \qquad \Delta G^{0^{\bullet}}_{et} small$

may be kinetically preferred because of the smaller $\Delta G^{0^{\star}}{}_{\mathrm{et}}$



































































(a) **Superexchange**: charge tunnels form the donor to the acceptor through the bridge in a nonadiabatic process. An exponential decrease in rate with increasing length of bridge is predicted.

(b) Hopping: charge occupies the bridge in traveling from donor to acceptor by hopping between discrete molecular orbitals on the bridge. If the rate of charge migration is faster than trapping, the charge should be able to migrate over long distances before getting trapped.

(c) **Domain Hopping:** charge occupies the bridge by delocalizing over several bases, or a domain. This domain hops along the bridge to travel from donor to acceptor. As in a pure hopping mechanism, the charge should be able to travel long distances before getting trapped.







Charge injection into a single G (12 to 14), charge transport to the complementary, radiolabeled strand (14 to 15), and charge transport from a single G + $^{\circ}$ to a GGG sequence (15 to 16). This assay is used to determine the relative rates and efficiencies of the charge transport from a single G+ $^{\circ}$ to a GGG sequence.













































Electro	n transfer transfer fo	parameter or differer	rs and ra nt donor-	te con -accep	stant tor pa	of elec irs.	ctron	Plot of k_{et} vs ΔG^0 for different donor-acceptor pairs obtained from transient absorption spectroscopy when donor molecules are enclosed within octa acid cavity.
Pairs	E(D/D ⁺) in CAN (eV)	E(D/D ⁺) in OA (eV)	E(A ^{2+/} A ^{·+}) in OA (eV)	E ₀₀ (eV)	$rac{e^2}{\varepsilon_S r_0}$ (eV)	ΔG^0 (eV)	$k_{et} {\rm (s^{-1})} \times 10^{-12}$	S. C.
C153+MV	0.89	0.505	-0.655	2.78	0.0209	-1.5991	0.0378	
C153+BV	0.89	0.505	-0.573	2.78	0.0203	-1.6817	0.0781	
Py+MV	1.4	1.015	-0.655	3.42	0.0209	-1.7291	0.116	4- 5 Solvert Separated BarlingLine Dair (SSDID)
An+MV	1.185	0.8	-0.655	3.22	0.0209	-1.7441	0.180	
Py+BV	1.4	1.015	-0.573	3.42	0.0203	-1.8117	0.227	$\lambda = 1.92 \text{ eV}$ 5 τ
An+BV	1.185	0.8	-0.573	3.22	0.0203	-1.8267	0.290	$v_{ei} = 0.0058 \text{ eV}$
C466+BV	0.92	0.535	-0.573	3.17	0.0203	-2.0417	0.370	
C480+MV	0.72	0.335	-0.655	3.06	0.0209	-2.0491	0.393	01 • `
C480+BV	0.72	0.335	-0.573	3.06	0.0203	-2.1317	0.400	-2.2 -2.0 -1.8 -1.6 -1.4
Gaz+MV	0.65	0.265	-0.655	3.3	0.0209	-2.3591	0.277	$\Delta G_0 (eV)$
Az+MV	0.71	0.325	-0.655	3.47	0.0209	-2.4691	0.250	

	transter to	or ditterer	nt donor.	-accep	tor pa	irs.	
Pairs	E(D/D ⁺) in CAN (eV)	E(D/D ⁺) in OA (eV)	E(A ^{2+/} A ^{·+}) in OA (eV)	E ₀₀ (eV)	$\frac{e^2}{\varepsilon_S r_0}$ (eV)	ΔG^0 (eV)	$k_{et} {\rm (s^{-1})} \times 10^{-12}$
C153+MV	0.89	0.505	-0.655	2.78	0.0209	-1.5991	0.0378
C153+BV	0.89	0.505	-0.573	2.78	0.0203	-1.6817	0.0781
Py+MV	1.4	1.015	-0.655	3.42	0.0209	-1.7291	0.116
An+MV	1.185	0.8	-0.655	3.22	0.0209	-1.7441	0.180

30

























	e 76-3 Halfwave Redox Potentials	of Aromatio	c Hydroi	carbons.		
No.	Compound	E ₁₀ (X ⁺ /X) (V vs. SCE) MeCN	Ref	E ₁₆ (X/X ⁻) (V vs. SCE) DMF	Ref	
1	Acenaphthene	+1.21	[6301]	-2.67	[7001]	HANDBOOK O
2	Acetylene, diphenyl-	-		-2.11	[7701]	PHOTOCHEMIST
3	Anthracene	+1.09	[6301]	-1.95	[7701]	THIRD EDITIO
4	Anthracene, 9,10-bis(phenylethynyl)-	+1.165	[6701]	-1.29	[6701]	THIRD EDITIO
5	Anthracene, 9,10-dimethyl-	+0.95	[6401]	-		
6	Anthracene, 9,10-diphenyl-	+1.22	[7701]	-1.94	[7701]	and the second se
7	Anthracene, 9-methyl-	+0.96	[6301]	-1.97 ^a	[6201]	100 M
8	Anthracene, 9-phenyl-	-		-1.86	[7001]	Contraction of the second seco
9	Azulene	+0.71	[6301]	-1.65 ^a	[6201]	Marco Montalti
10	Benz[a]antracene	+1.18	[6301]	-		Autorio Crean Luca Prodi M. Teresa Gandolfi with introductory sections by Josef Michd and Vincence
Tabl	le 7b-7 Halfwave Redox Potentials	of Nitriles.				
No.	Compound	(V)	E _% (A/A ⁻ vs. Ag elec DMF ^a) E _% (trode) (V v M	(A/A*) 15. SCE) IeCN	e la constante de la constante
1	Anthracene, 9-cyano-		-	-1	1.58 ^b	Chapter 7
2	Anthracene, 9,10-dicyano-		-	-4	0.98 ^b	Chapter /
3	Benzene, 1-cyano-3,5-dinitro-		-0.96		-	
4	Benzene, 1-cyano-4-nitro-		-1.25		-	
ż	Benzene 12 diarane		2.12			







Developing a scalable artificial photosynthesis technology through nanomaterials by design <u>Nathan S. Lewis</u> *Nature Nanotechnology* **2016**, *11*, 1010–1019 The photoanode material absorbs blue light and effects water oxidation. The photocathode material absorbs red light and drives the reduction of water or carbon dioxide. The photoanode and photocathode material are in ohmic contact, and both photoelectrodes are decorated with catalysts for the reaction of interest. The membrane allows for the transfer of ions and separates the products.



Highly active cobalt phosphate and borate based oxygen evolving catalysts operating in neutral and natural waters[†]

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PAPER



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Fig. 1 Dried catalyst films formed under (a) quiescent (0.85 V ts. Ag/ AgCl) and (b) catalytically active (1.1 V ts. Ag/AgCl) conditions on an ITO substrate. Environmental "wet" SEM images (c) at 3500x and (d) 10 000x magnification of Co-OEC films deposited at 1.1 V ts. Ag/AgCl on a Ni foil substrate. (a) and (b) reproduced from ref. 22 with permission from the Royal Society of Chemistry.





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