Redox reactions

Oxidation/reduction reactions

- **Electron transfer reactions**
  - – Redox couples & half reactions
    - One component is reduced (accepts electron(s))
    - One component is oxidized (donates electron(s))

$$A + e^- \leftrightarrow A^*$$

$$B + e^- \leftrightarrow B^*$$

$$\boldsymbol{B} + \boldsymbol{A}^* \rightarrow \boldsymbol{B}^* + \boldsymbol{A}$$

  - – Most natural organic compounds are (primarily) electron donors

Oxidation/reduction reactions

- **Most important biotic reactions**
  - Primary energy source
    - Cell maintenance
    - Cell growth

ex) glucose oxidation mediated by microorganisms

$$\frac{1}{4}CO_2 + H^+ + e^- \rightarrow \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \qquad \text{(A)}$$

$$\frac{1}{4}O_2 + H^+ + e^- \rightarrow \frac{1}{2}H_2O \qquad \text{(B)}$$

24 x [(B)-(A)] $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Oxidation/reduction reactions

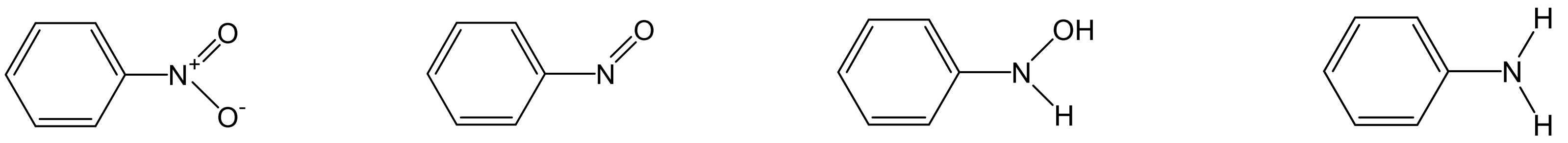
- **Photochemical reactions**
  - Will discuss later

- **Redox reactions also occur abiotically in the dark**
  - May involve mediators/catalysts
  - Although the reaction itself is abotic, biological molecules can be involved

Abiotic redox rxn mediated by NOM

- **Nitrobenzene reduction**
  - Nitrobenzene ($C_6H_5NO_2$) may be reduced in a stepwise manner to be transformed into aniline ($C_6H_5NH_2$) in the environment

$$ArNO_2 \xrightarrow[-H_2O]{+2e^- + 2H^+} ArNO \xrightarrow{+2e^- + 2H^+} ArNHOH \xrightarrow[-H_2O]{+2e^- + 2H^+} ArNH_2$$



oxidation state: ***N(   )*** ***N(   )*** ***N(   )*** ***N(   )***

** Ar denotes C_6H_5-*

Abiotic redox rxn mediated by NOM

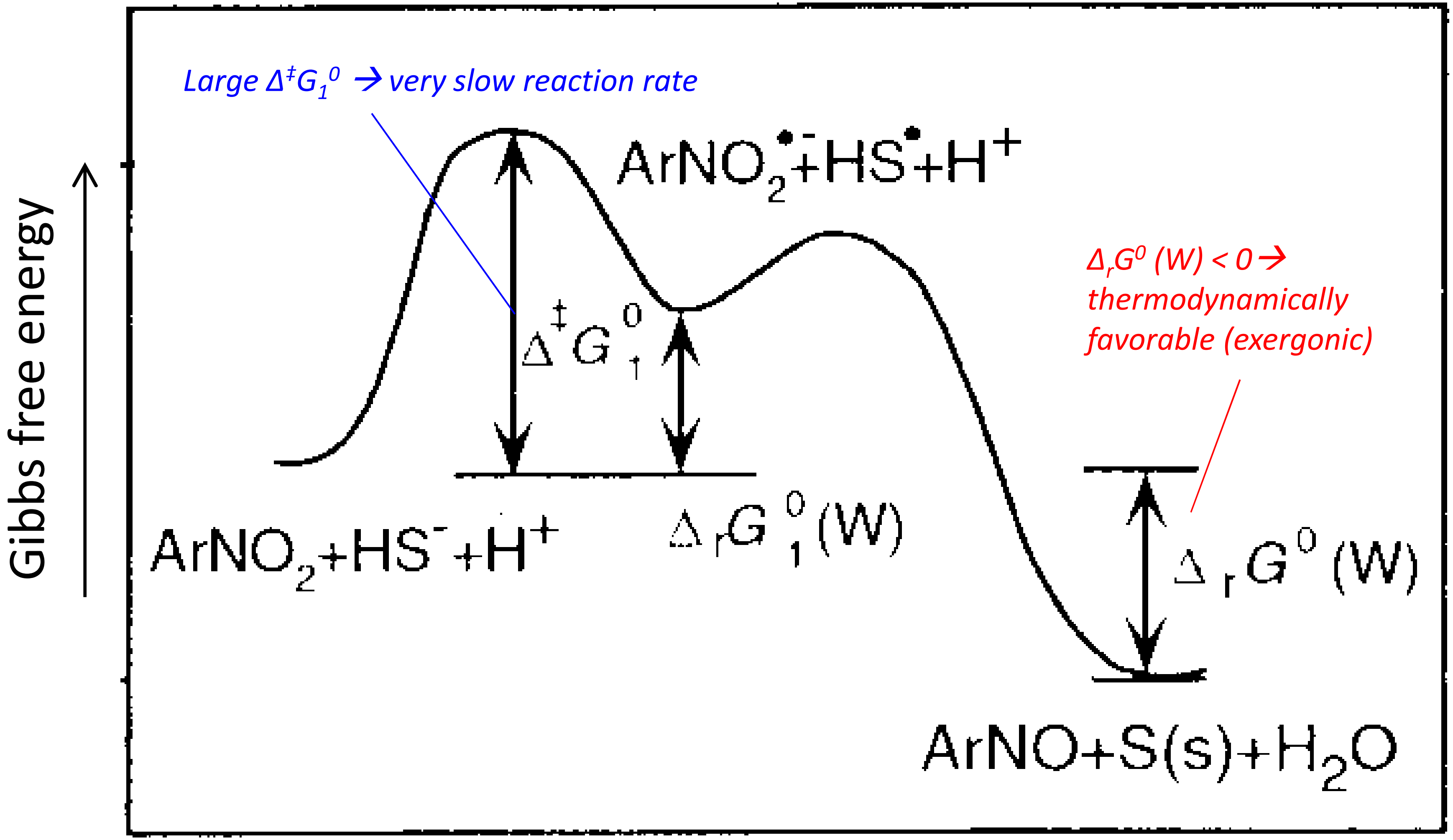
Let's consider the first step with hydrogen sulfide (H_2S) *as an oxidizing compound (reductant)*

Reduction half-rxn: $ArNO_2 + 2e^- + 2H^+ \longrightarrow ArNO + H_2O$

Oxidation half-rxn: $H_2S(aq) = HS^-(aq) + H^+ \longrightarrow S(s) + 2e^- + 2H^+$

Overall rxn: $ArNO_2 + H_2S(aq) \longrightarrow ArNO + S(s) + H_2O$

Abiotic redox rxn mediated by NOM

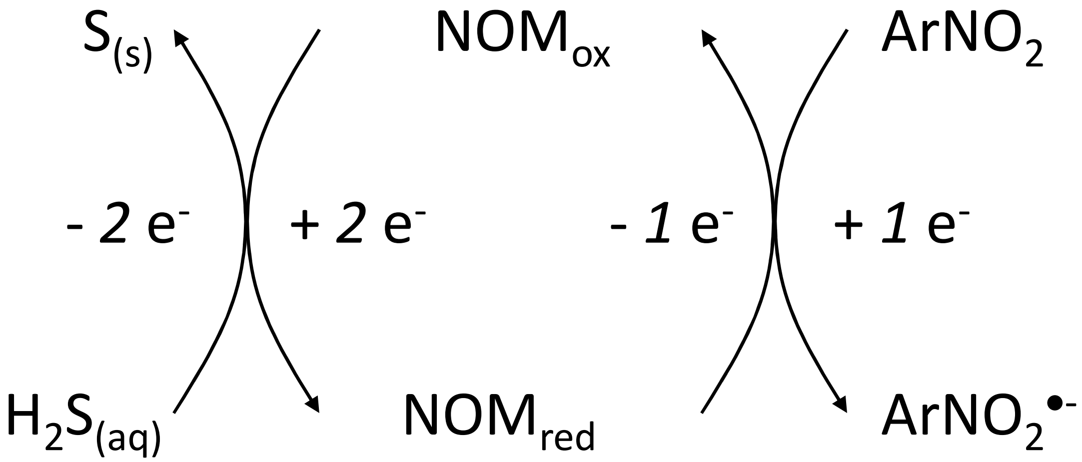


Large $\Delta^{\ddagger}G_1^0$ → very slow reaction rate

$\Delta_r G^0$ (W) < 0 → thermodynamically favorable (exergonic)

Abiotic redox rxn mediated by NOM

- **Natural organic matter (NOM) acts as e^- transfer mediators**

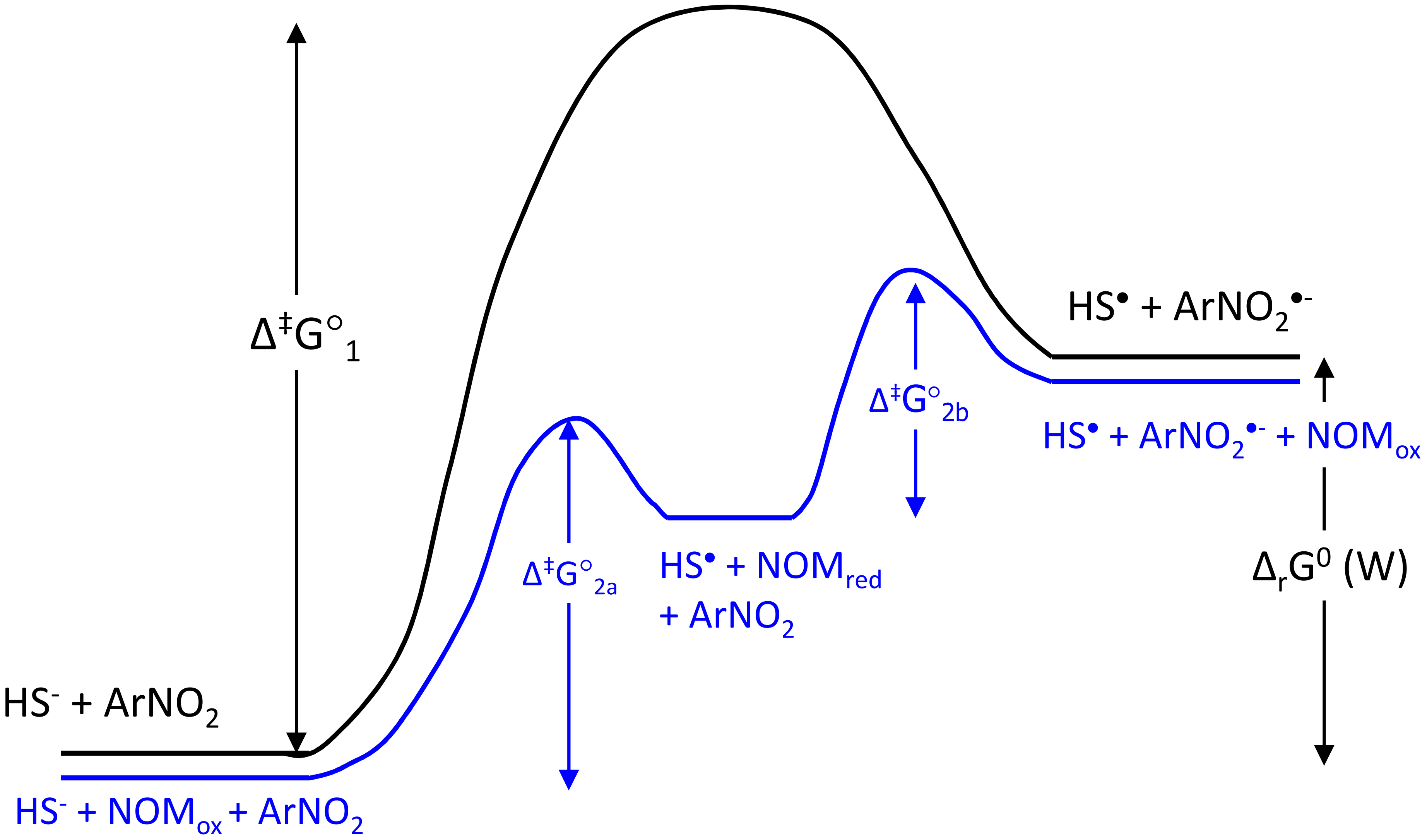


$S_{(s)}$ NOM_{ox} $ArNO_2$

$-\,2\ e^-$ $+\,2\ e^-$ $-\,1\ e^-$ $+\,1\ e^-$

$H_2S_{(aq)}$ NOM_{red} $ArNO_2^{\bullet-}$

- So ultimately electrons flow from H_2S to $ArNO_2$



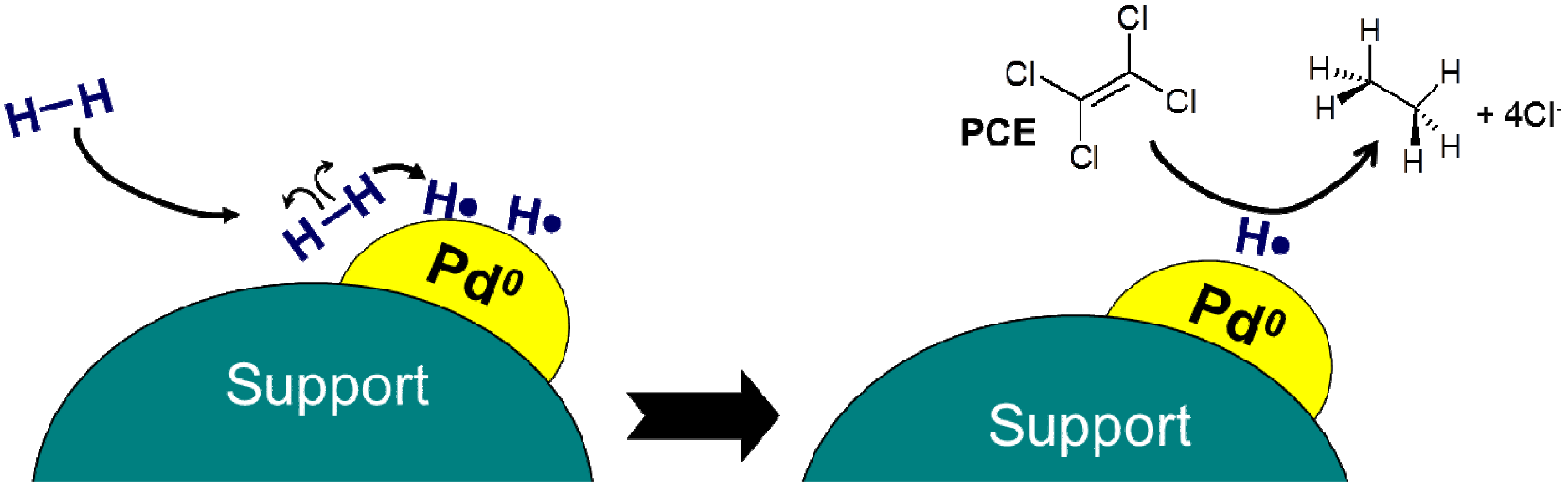
- By e^- transfer by NOM, the activation energy for the rate-limiting step is reduced → reaction proceeds faster

Pd-catalyzed hydrodehalogenation

Net reaction:

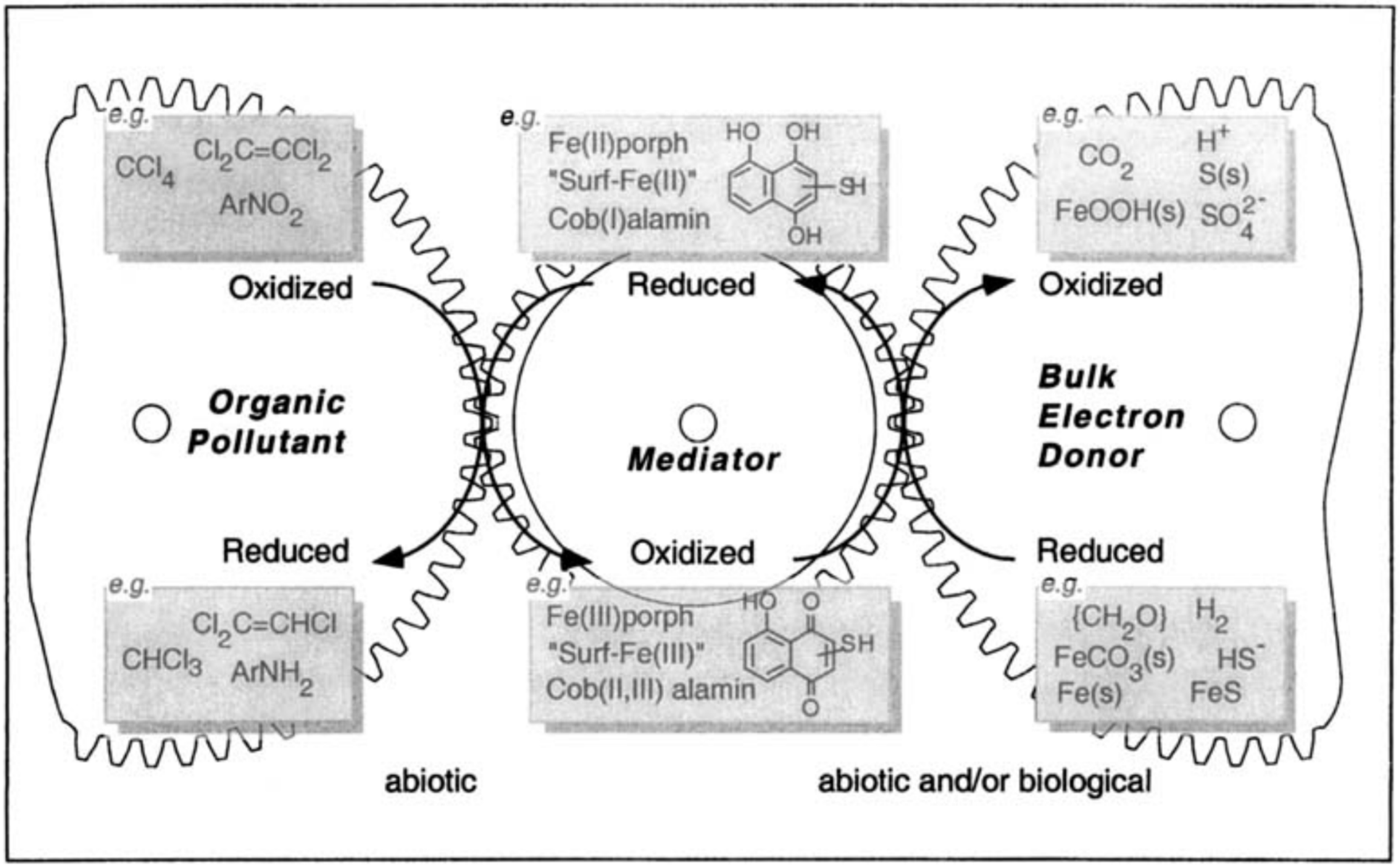
$$Cl_2C = CCl_2 \quad + \quad 5H_2 \xrightarrow{\boxed{\textbf{Pd}}} H_3C - CH_3 \; + 4H^+ + 4Cl^-$$

PCE ethane



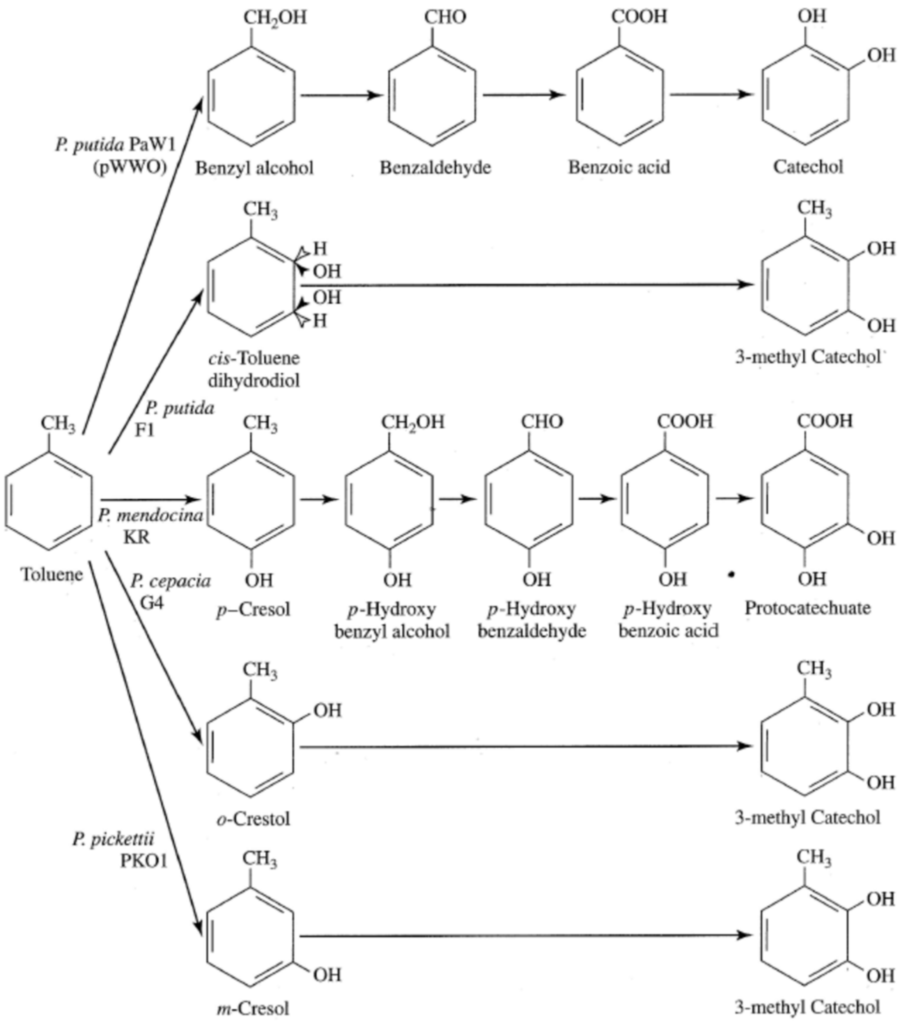
- Pd dissociates H_2 molecules
- Rapid reduction of TCE at the surface of Pd

Reduction of organics by biomolecules



Redox reactions – multiple pathways

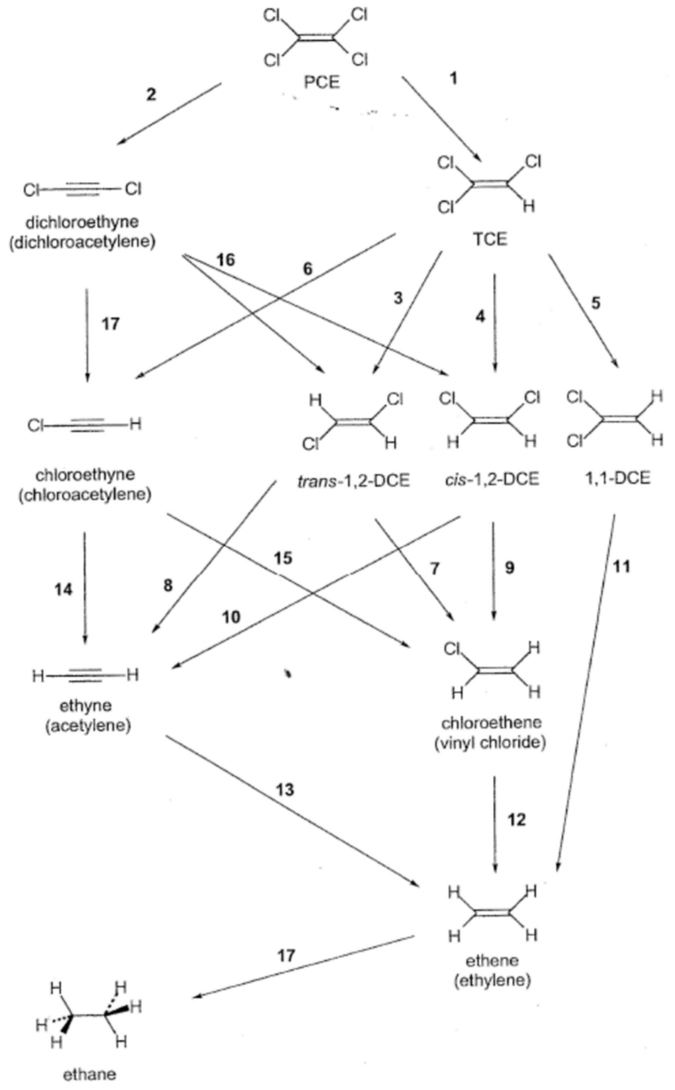
- **Aerobic microbial transformation of toluene**



Five different aerobic biodegradation pathways for toluene, each initiated through the activity of a mono- or di-oxygenase together with molecular oxygen. (Mikesell et al., 1993)

Redox reactions – multiple pathways

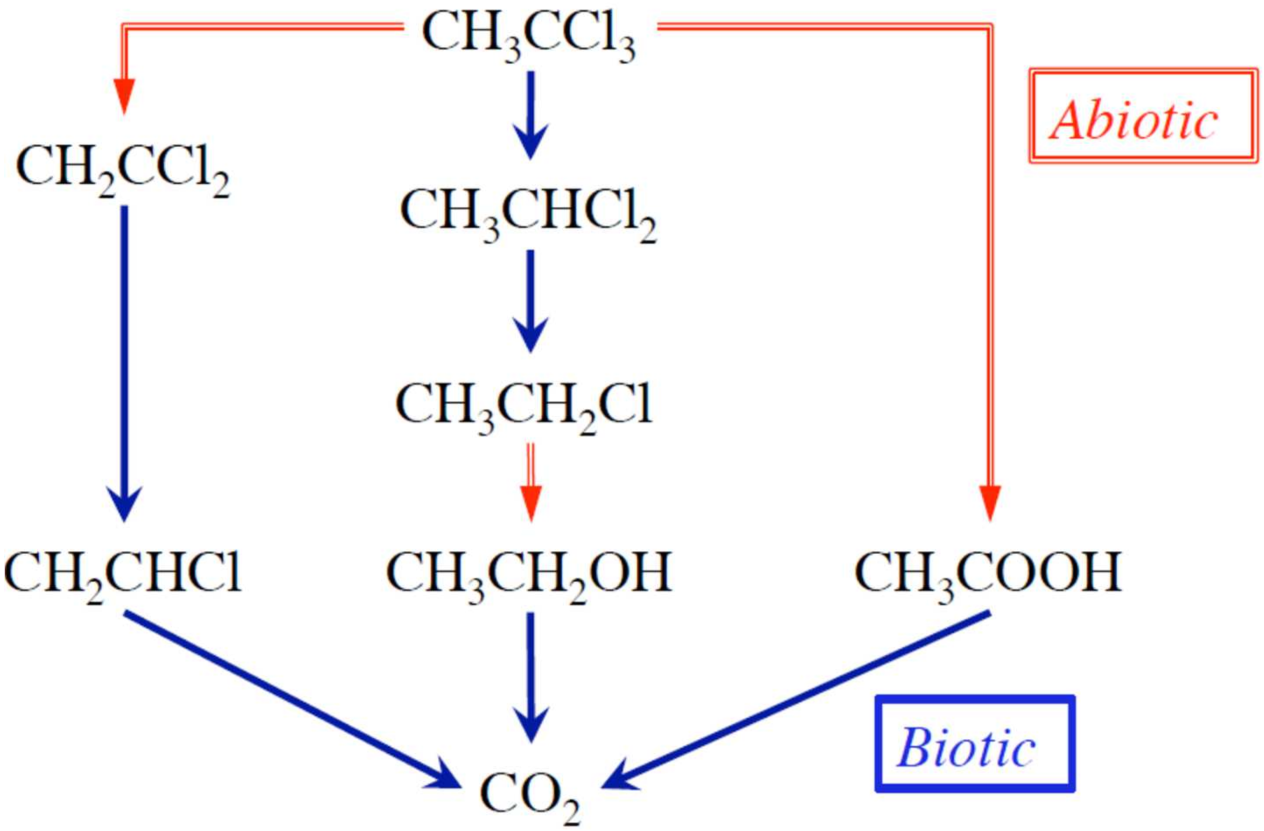
- **Anaerobic PCE reaction pathways with zero valent iron (Fe^0) (abiotic)**



Hypothesized reaction sequence for reduction of chlorinated ethenes and related compounds by Fe^0. Adapted from Arnold and Roberts (2000).

Redox reactions – multiple pathways

- **Methanogenic TCA transformations: abiotic-biotic combination**



CH_3CCl_3

CH_2CCl_2

CH_3CHCl_2

CH_3CH_2Cl

CH_2CHCl

CH_3CH_2OH

CH_3COOH

CO_2

Abiotic

Biotic

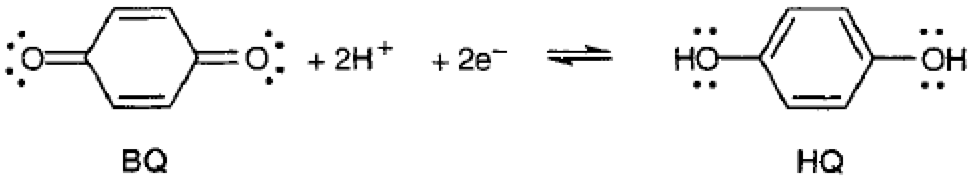
Adapted from
Vogel et al. (1987)

Thermodynamics of redox reactions

- **Thermodynamics of a redox reaction tell us if the reaction will proceed**
  - If $\Delta G_r < 0$, exergonic, the reaction will proceed
  - If $\Delta G_r > 0$, endergonic, the reaction is not likely to proceed
- **It is useful to prepare a list of free energy change of half reactions**
  - You can pick up a pair of reduction/oxidation half reactions from the list, and then combine $\Delta G_{r\,(reduction)}$ & $\Delta G_{r\,(oxidation)}$ to obtain $\Delta G_{r\,(overall)}$
- **How do we determine ΔG_r of half reactions by experiments?**

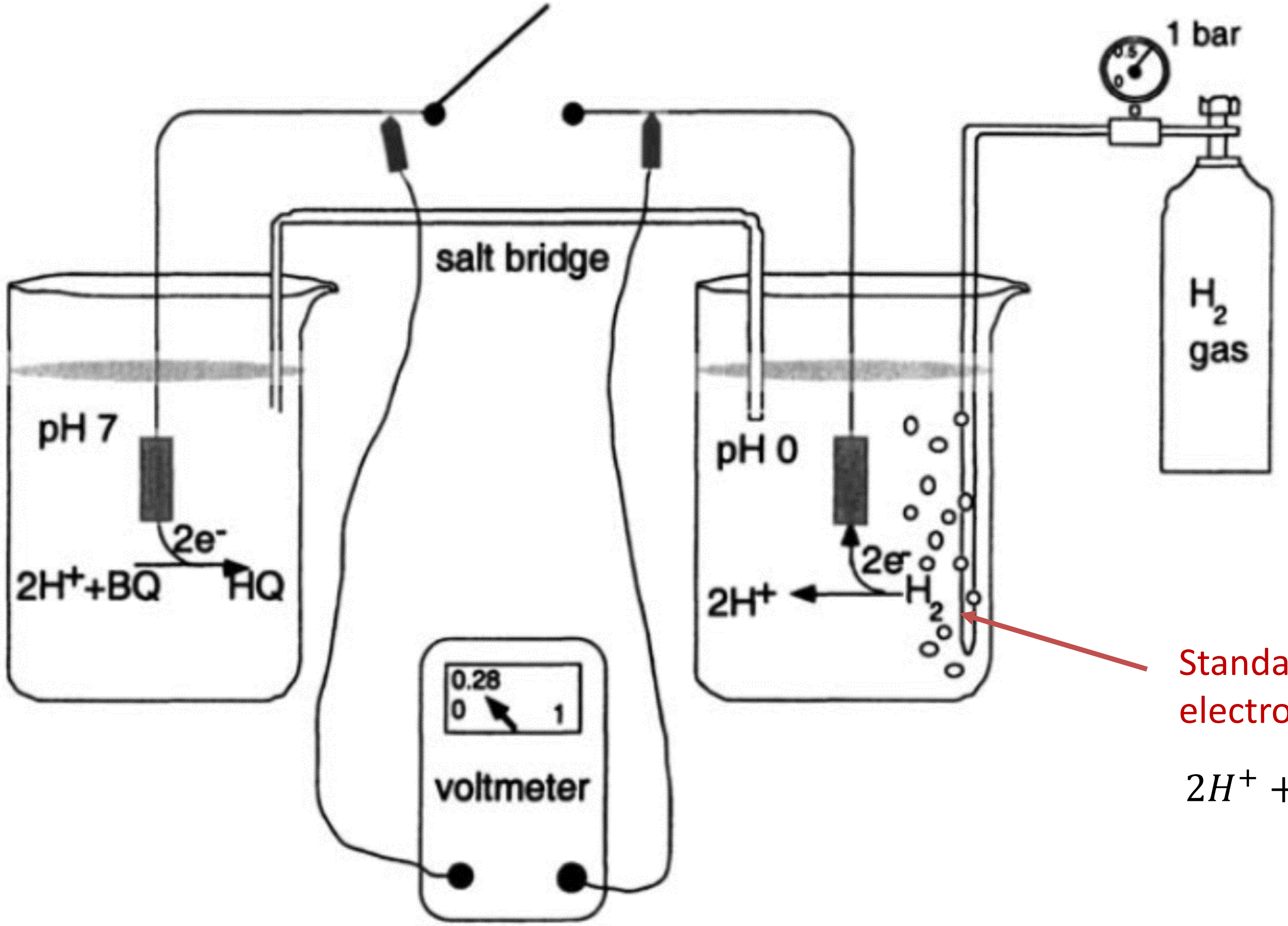
Thermodynamics of redox reactions

- **Consider a reversible reaction to convert 1,4-benzoquinone (BQ) to hydroquinone (HQ):**



- **Use reduction potentials for evaluating the free energy of the half reaction**
  - Perform the reaction at the surface of an inert electrode (ex: platinum, graphite)
  - At the other side, another inert electrode is immersed in an aqueous solution maintained at pH 0 (i.e., $\{H^+\} = 1$) and bubbled with molecular hydrogen ($p_{H_2} = 1\ bar$) – standard hydrogen electrode (SHE)

Thermodynamics of redox reactions



Standard hydrogen electrode (SHE)

$$2H^+ + 2e^- \rightleftharpoons H_2(g)$$

Thermodynamics of redox reactions

- **Overall reaction:**

$$BQ + H_2(g) + 2H^+ \rightleftharpoons HQ + 2H^+$$

1 bar (at SHE)

pH=7 (prev. example)

pH=0 (at SHE)

- **With half reactions:**
  - BQ ↔ HQ electrode: $BQ + 2H^+ + 2e^- \rightleftharpoons HQ$
  - SHE: $2H^+ + 2e^- \rightleftharpoons H_2(g)$

Thermodynamics of redox reactions

- **Relationship between the electrical potential and the free energy**
  - Assuming electrochemical equilibrium at the electrode surface, then the potential difference, *ΔE*, is directly related to the free energy change, $\Delta_r G$ of the reaction:

$$\boxed{\Delta_r G = -nF\Delta E}$$

n = number of electrons transferred

F = Faraday constant, 96485 Coulomb/mol

= 96.5 kJ/mol-V

- **At the SHE**
  - We assign a zero value of electrical potential, and thus, a zero value of a standard free energy change:

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2(g) \qquad \Delta E^0 = 0\,V, \qquad \Delta_r G^0 = 0\ kJ/mol$$

  - Then, the electrical potential change of the half reaction, $BQ + 2H^+ + 2e^- \rightleftharpoons HQ$, can be directly measured by the electrical potential change at the galvanic cell

Thermodynamics of redox reactions

- **The electrical potential relative to SHE, E_H**

$$\boxed{E_H = -\frac{\Delta_r G}{nF}}$$

- **The E_H value for any conditions other than the "standard" state**
  - The free energy change of a reaction ($\Delta_r G$) at any conditions is given as

$$\Delta_r G = \Delta_r G^0 + RT ln Q_r$$

$$\boxed{E_H = E_H{}^0 - \frac{RT}{nF} ln Q_r = E_H{}^0 - \frac{2.303RT}{nF} log Q_r}$$

$E_H{}^0$ = standard redox potential or standard reduction potential (E_H at 25°C with unit (1) activities for all reaction components)

Q_r = reaction quotient

for reaction aA + bB = cC + dD,

$$Q_r = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$

Conditions for E_H^0 & E_H^0 (W)

- **E_H^0**
  - All reaction components have unit activities
- **E_H^0 (W)**
  - E_H under **typical natural water conditions**:
    - pH = 7
    - $[Cl^-] = 10^{-3}$ M; $[Br^-] = 10^{-5}$ M
    - Organic oxidant and reductant have unit activities

$\Delta_r G^0$ & $\Delta_r G^0$ *(W)* and $E_H{}^0$ & $E_H{}^0$ *(W)*

Q: Consider the half reaction in an aqueous solution:

$$2NO_3{}^- + 12H^+ + 10e^- \rightleftharpoons N_2(g) + 6H_2O \qquad \text{(denitrification)}$$

$$\Delta_r G^0 = -1200\ kJ/mol$$

Calculate the $E_H{}^0$, $E_H{}^0$ *(W)*, and $\Delta_r G^0$ *(W)* values of the reaction.

Thermodynamics of redox reactions

- **The overall free energy change of a redox reaction:**

  Reduction: EA + e^- → reduced EA $\Delta_{red}G^0$

  Oxidation: ED → oxidized ED + e^- $\Delta_{oxi}G^0$

  EA + ED → reduced EA + oxidized ED $\Delta_{r}G^0$

  $\Delta_r G^0 = \Delta_{red}G^0 + \Delta_{oxi}G^0$

  - Under the standard conditions:
    - Negative $\Delta_r G^0$: <u>favorable</u> reaction
    - Large $|\Delta_r G^0|$ (with $\Delta_r G^0 < 0$): strong <u>driving force</u> for the forward reaction, makes the backward reaction difficult
    - Note: this is thermodynamics, **<u>NOT</u>** kinetics!

Applying thermodynamics – simple example

ΔG⁰(W)/e⁻, *kJ/mol*

A	$2H^{+} + 2e^{-} \leftrightarrow H_2\,(g)$	*+40.0*
B	$O_2\,(g) + 4H^{+} + 4e^{-} \leftrightarrow 2H_2O$	*-78.3*

B-2A $2H_2\,(g) + O_2\,(g) \leftrightarrow 2H_2O$

$$\Delta_r G^0 = 4 \times (-78.3 - 40.0)$$
$$= -473.2\ kJ/mol\ O_2$$

The equilibrium constant for this reversible reaction:

$$K = \frac{1}{P_{O_2} {P_{H_2}}^2}$$

Applying thermodynamics – simple example

Recall $\Delta_r G = \Delta_r G^0 + RTln(Q_r)$

at equilibrium, $\Delta_r G = 0$ and $Q_r = K$

$$\Rightarrow \quad \Delta_r G^0 = -RTln(K)$$

Therefore, $K = \dfrac{1}{P_{O_2} {P_{H_2}}^2} = e^{-\left(\Delta_r G^0 / RT\right)} \approx 10^{83}$

The overall reaction will proceed to the right at any reasonable partial P of H_2 & O_2

E_H & Δ_rG of some important redox rxns

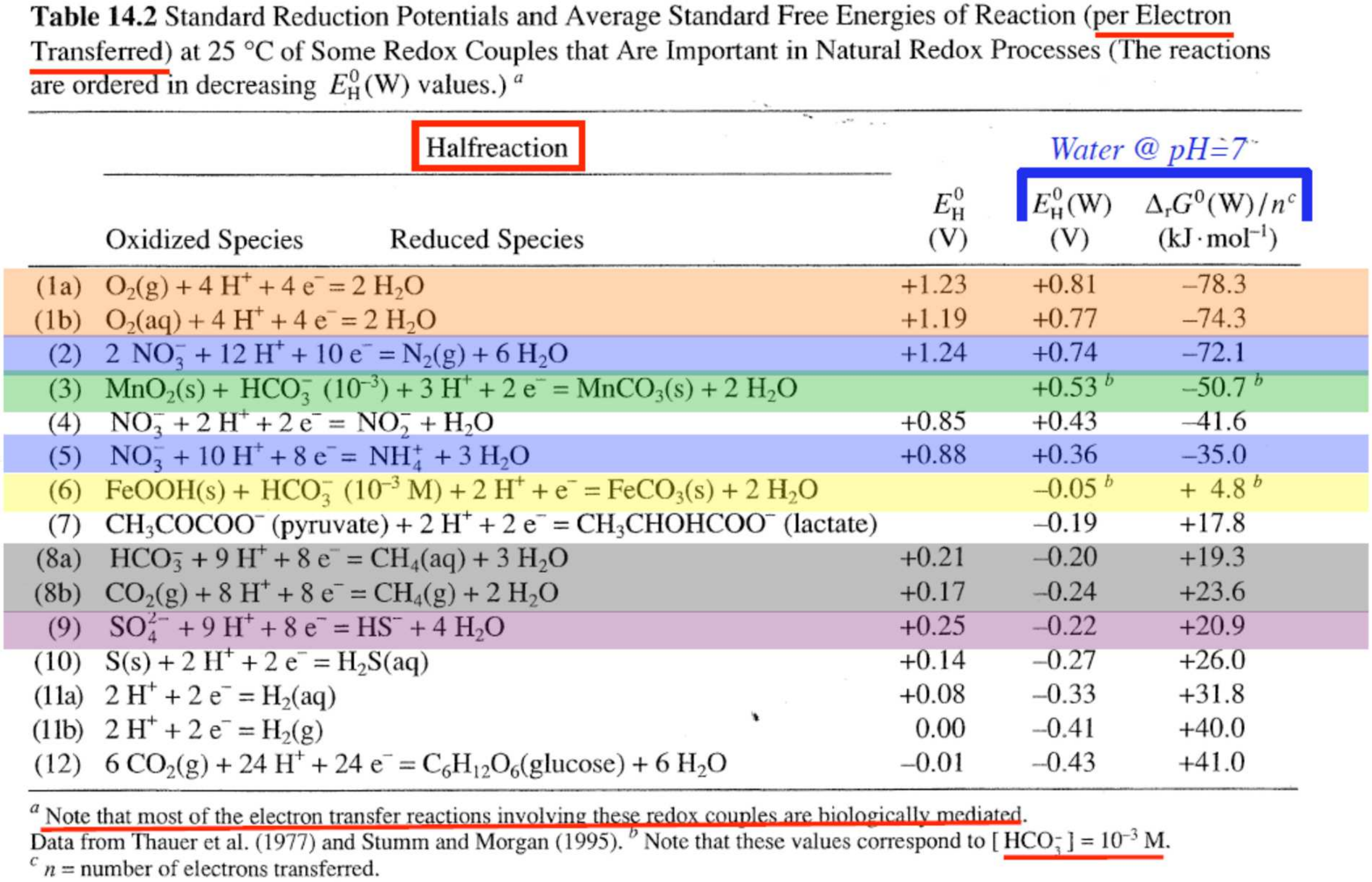
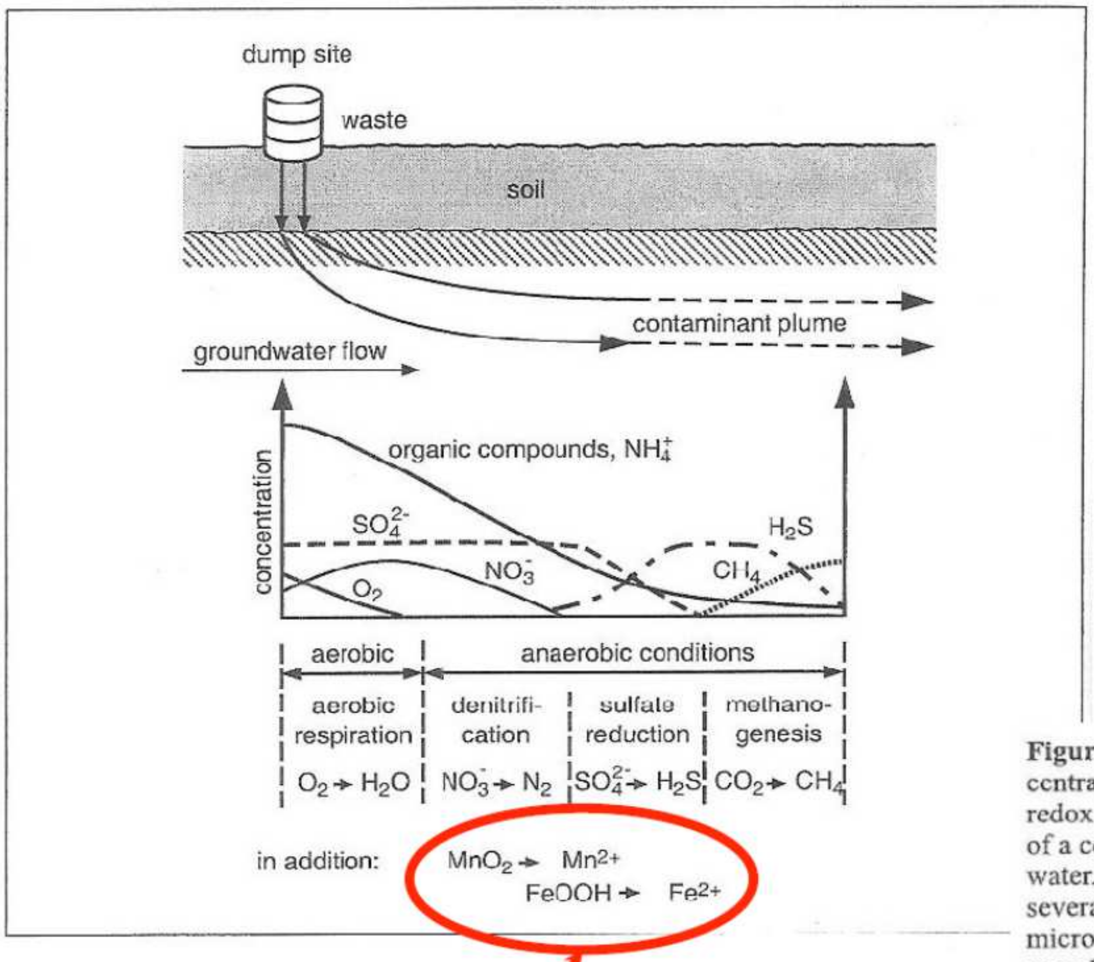


Table 14.2 Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25 °C of Some Redox Couples that Are Important in Natural Redox Processes (The reactions are ordered in decreasing E_H^0(W) values.)[a]

	Halfreaction		Water @ pH≐7	
	Oxidized Species Reduced Species	E_H^0 (V)	$E_H^0(W)$ (V)	$\Delta_rG^0(W)/n^c$ ($kJ \cdot mol^{-1}$)
(1a)	$O_2(g) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.23	+0.81	–78.3
(1b)	$O_2(aq) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.19	+0.77	–74.3
(2)	$2\,NO_3^- + 12\,H^+ + 10\,e^- = N_2(g) + 6\,H_2O$	+1.24	+0.74	–72.1
(3)	$MnO_2(s) + HCO_3^-\ (10^{-3}) + 3\,H^+ + 2\,e^- = MnCO_3(s) + 2\,H_2O$		+0.53[b]	–50.7[b]
(4)	$NO_3^- + 2\,H^+ + 2\,e^- = NO_2^- + H_2O$	+0.85	+0.43	–41.6
(5)	$NO_3^- + 10\,H^+ + 8\,e^- = NH_4^+ + 3\,H_2O$	+0.88	+0.36	–35.0
(6)	$FeOOH(s) + HCO_3^-\ (10^{-3}\ M) + 2\,H^+ + e^- = FeCO_3(s) + 2\,H_2O$		–0.05[b]	+ 4.8[b]
(7)	CH_3COCOO^- (pyruvate) $+ 2\,H^+ + 2\,e^- = CH_3CHOHCOO^-$ (lactate)		–0.19	+17.8
(8a)	$HCO_3^- + 9\,H^+ + 8\,e^- = CH_4(aq) + 3\,H_2O$	+0.21	–0.20	+19.3
(8b)	$CO_2(g) + 8\,H^+ + 8\,e^- = CH_4(g) + 2\,H_2O$	+0.17	–0.24	+23.6
(9)	$SO_4^{2-} + 9\,H^+ + 8\,e^- = HS^- + 4\,H_2O$	+0.25	–0.22	+20.9
(10)	$S(s) + 2\,H^+ + 2\,e^- = H_2S(aq)$	+0.14	–0.27	+26.0
(11a)	$2\,H^+ + 2\,e^- = H_2(aq)$	+0.08	–0.33	+31.8
(11b)	$2\,H^+ + 2\,e^- = H_2(g)$	0.00	–0.41	+40.0
(12)	$6\,CO_2(g) + 24\,H^+ + 24\,e^- = C_6H_{12}O_6$(glucose) $+ 6\,H_2O$	–0.01	–0.43	+41.0

[a] Note that most of the electron transfer reactions involving these redox couples are biologically mediated. Data from Thauer et al. (1977) and Stumm and Morgan (1995). [b] Note that these values correspond to $[HCO_3^-] = 10^{-3}$ M.
[c] n = number of electrons transferred.

Oxidation cascade



Mineral oxidation/reduction

Figure 14.3 Variation in concentrations of important dissolved redox species along the flowpath of a contaminant plume in groundwater. This sequence results in several zones of characteristic microbial metabolism and corresponding redox conditions (adapted from Bouwer et al., 1984).

Oxidation cascade – why?

	$\Delta_r G^0(W)$ (kJ/mol glucose)
$C_6H_{12}O_6 + \boxed{6O_2} \Rightarrow 6CO_2 + 6H_2O$	-2863.2
$C_6H_{12}O_6 + \boxed{4.8NO_3{}^-} + 4.8H^+ \Rightarrow 6CO_2 + 2.4N_2 + 8.4H_2O$	-2714.4
$C_6H_{12}O_6 + \boxed{24FeOOH(s)} + 24HCO_3{}^- + 24H^+ \Rightarrow 6CO_2 + 24FeCO_3 + 42H_2O$	-868.8
$C_6H_{12}O_6 + \boxed{3SO_4{}^{2-}} + 3H^+ \Rightarrow 6CO_2 + 3HS^- + 6H_2O$	-482.4
$C_6H_{12}O_6 \Rightarrow 3CO_2 + 3CH_4$	-417.6

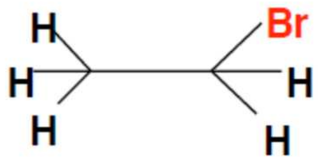
e^- acceptor: CO_2

- More energy/substrate means that more of the substrate can be used to make new cells
- The electron acceptor that generates the most energy get used up first

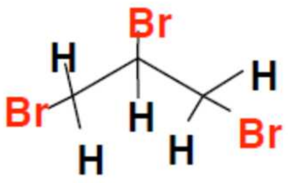
Halogenated aliphatic hydrocarbons

- **Heavily used:**
  - As solvents
  - As pesticides
  - For fire control
- **Halogens affect:**
  - Size
  - C oxidation state

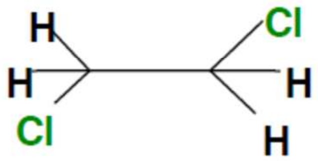
BROMOETHANE



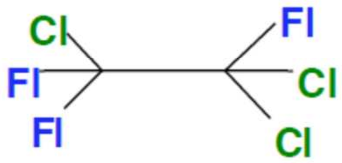
DBCP



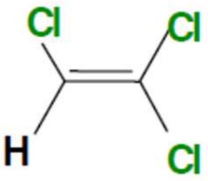
1,2-DICHLOROETHANE



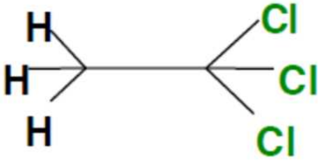
CFC-113



TRICHLOROETHYLENE



1,1,1-TRICHLOROETHANE



Halogenated aliphatic hydrocarbons

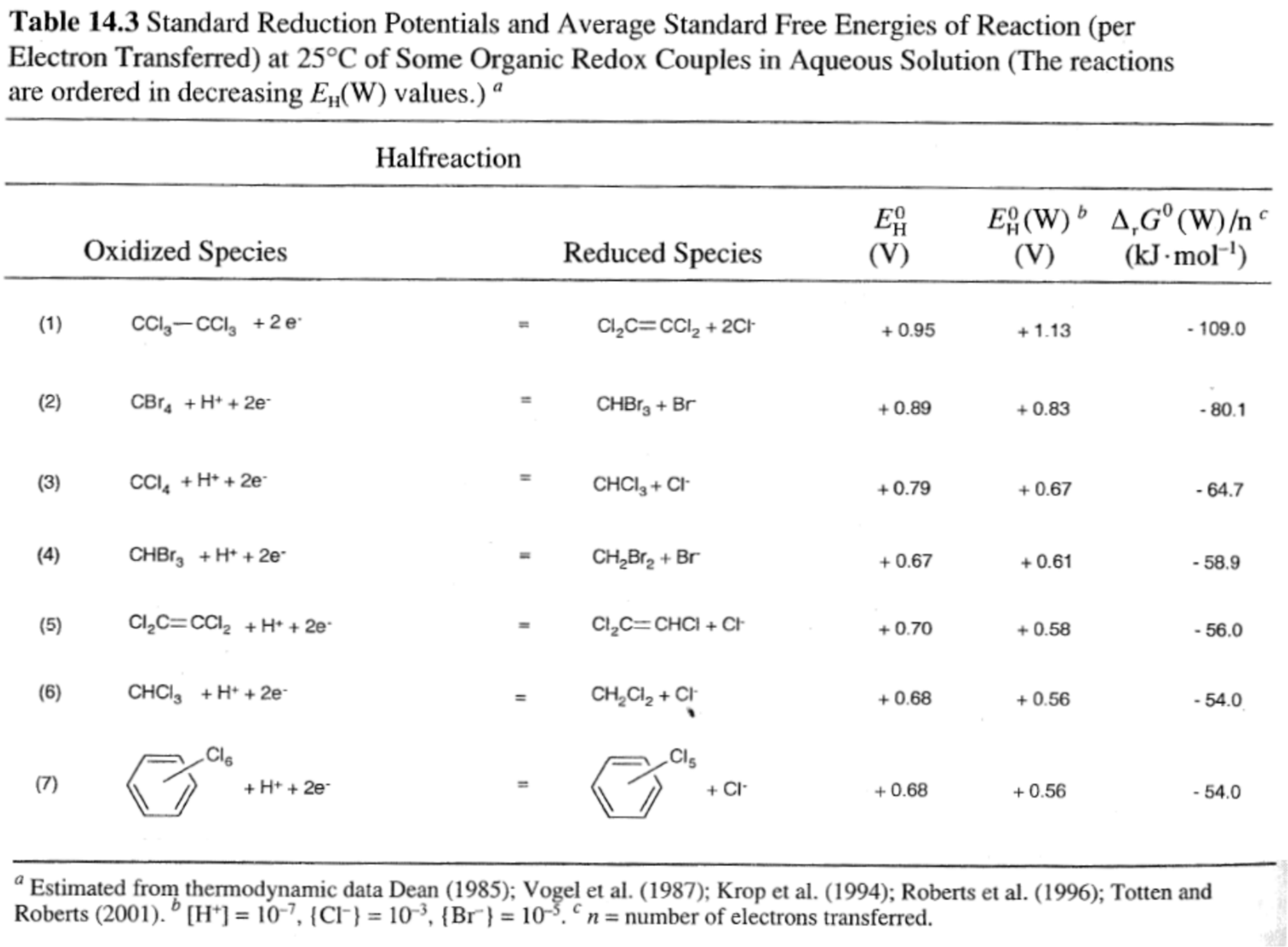
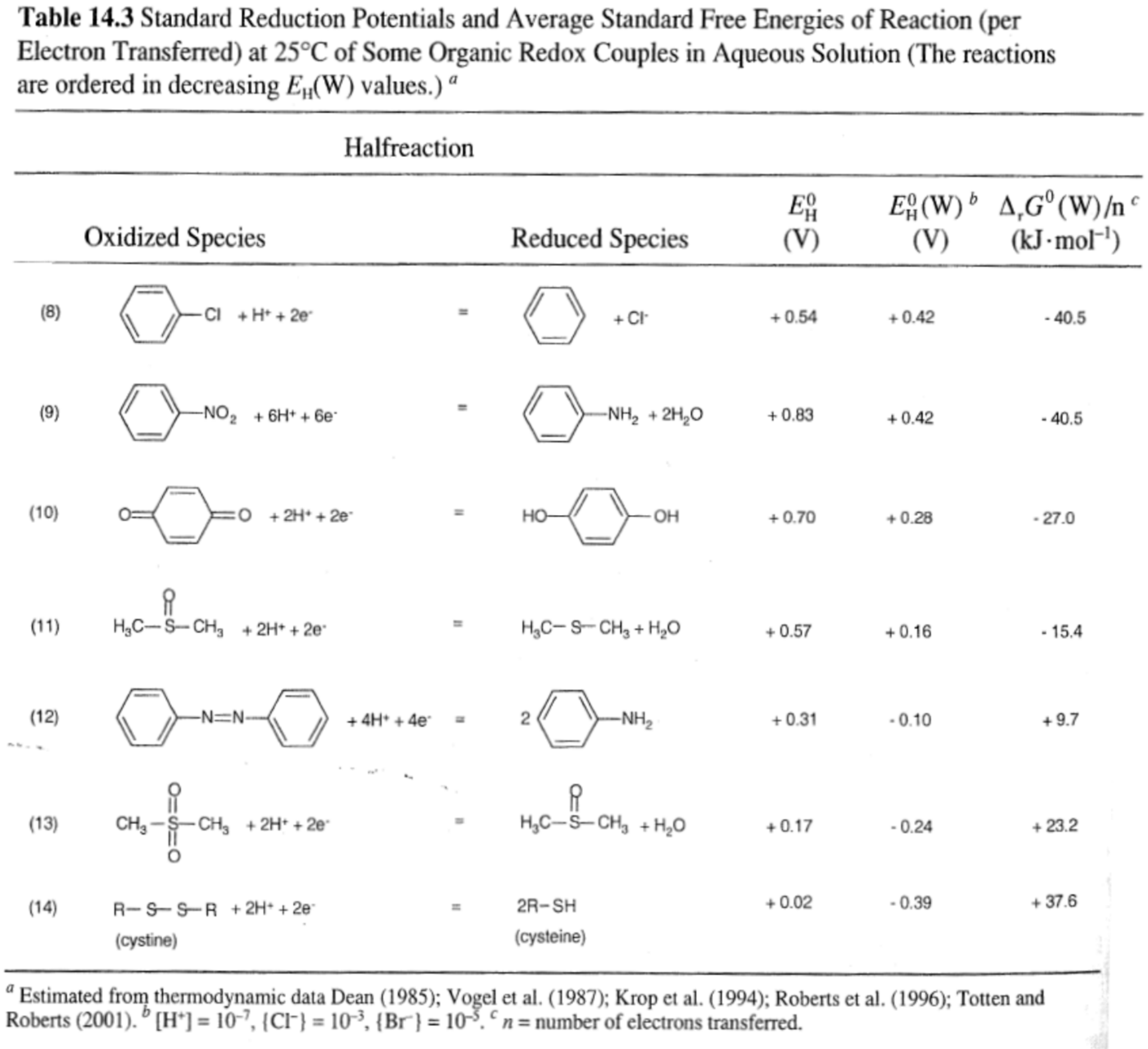


Table 14.3 Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25°C of Some Organic Redox Couples in Aqueous Solution (The reactions are ordered in decreasing E_H(W) values.) [a]

	Halfreaction					
	Oxidized Species		Reduced Species	E_H^0 (V)	$E_H^0(W)$ [b] (V)	$\Delta_r G^0(W)/n$ [c] ($kJ \cdot mol^{-1}$)
(1)	$CCl_3-CCl_3 + 2e^-$	=	$Cl_2C=CCl_2 + 2Cl^-$	+ 0.95	+ 1.13	- 109.0
(2)	$CBr_4 + H^+ + 2e^-$	=	$CHBr_3 + Br^-$	+ 0.89	+ 0.83	- 80.1
(3)	$CCl_4 + H^+ + 2e^-$	=	$CHCl_3 + Cl^-$	+ 0.79	+ 0.67	- 64.7
(4)	$CHBr_3 + H^+ + 2e^-$	=	$CH_2Br_2 + Br^-$	+ 0.67	+ 0.61	- 58.9
(5)	$Cl_2C=CCl_2 + H^+ + 2e^-$	=	$Cl_2C=CHCl + Cl^-$	+ 0.70	+ 0.58	- 56.0
(6)	$CHCl_3 + H^+ + 2e^-$	=	$CH_2Cl_2 + Cl^-$	+ 0.68	+ 0.56	- 54.0
(7)	Cl_6 $+ H^+ + 2e^-$	=	Cl_5 $+ Cl^-$	+ 0.68	+ 0.56	- 54.0

[a] Estimated from thermodynamic data Dean (1985); Vogel et al. (1987); Krop et al. (1994); Roberts et al. (1996); Totten and Roberts (2001). [b] $[H^+] = 10^{-7}$, $\{Cl^-\} = 10^{-3}$, $\{Br^-\} = 10^{-5}$. [c] n = number of electrons transferred.

Halogenated aliphatic hydrocarbons



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	Halfreaction					
	Oxidized Species		Reduced Species	E_H^0 (V)	E_H^0(W) [b] (V)	$\Delta_r G^0$(W)/n [c] (kJ·mol^{-1})
(8)	—Cl $+ H^+ + 2e^-$	=	$+ Cl^-$	+ 0.54	+ 0.42	- 40.5
(9)	—NO_2 $+ 6H^+ + 6e^-$	=	—NH_2 $+ 2H_2O$	+ 0.83	+ 0.42	- 40.5
(10)	O= =O $+ 2H^+ + 2e^-$	=	HO— —OH	+ 0.70	+ 0.28	- 27.0
(11)	$H_3C-\overset{O}{\overset{\parallel}{S}}-CH_3$ $+ 2H^+ + 2e^-$	=	$H_3C-S-CH_3 + H_2O$	+ 0.57	+ 0.16	- 15.4
(12)	—N=N— $+ 4H^+ + 4e^-$	=	2 —NH_2	+ 0.31	- 0.10	+ 9.7
(13)	$CH_3-\underset{O}{\overset{O}{S}}-CH_3$ $+ 2H^+ + 2e^-$	=	$H_3C-\overset{O}{\overset{\parallel}{S}}-CH_3$ $+ H_2O$	+ 0.17	- 0.24	+ 23.2
(14)	$R-S-S-R$ $+ 2H^+ + 2e^-$ (cystine)	=	2R−SH (cysteine)	+ 0.02	- 0.39	+ 37.6

[a] Estimated from thermodynamic data Dean (1985); Vogel et al. (1987); Krop et al. (1994); Roberts et al. (1996); Totten and Roberts (2001). [b] $[H^+] = 10^{-7}$, $\{Cl^-\} = 10^{-3}$, $\{Br^-\} = 10^{-3}$. [c] n = number of electrons transferred.

Reductive dechlorination of C_2Cl_6

	***E_H^0**, V*	***$\Delta_r G^0$**, kJ/mol* *$=-nFE_H^0$*
Eq. (1) of Table 14.3:		
$C_2Cl_6 + 2e^- \rightarrow C_2Cl_4 + 2Cl^-$	*0.95*	*-183.4*
Couple with Eq. 11b of Table 14.2:		
$2H^+ + 2e^- \rightarrow H_2$	*0*	*0*

Overall reaction:

$$C_2Cl_6 + H_2 \rightarrow C_2Cl_4 + 2H^+ + 2Cl^-$$

$$\Delta_r G^0 = -183.4 - 0 = -183.4\ kJ/mol\ C_2Cl_6$$

$$\Delta_r G^0 = -RTlnK$$

$$K = e^{-\Delta_r G^0/RT} = 1.4 \times 10^{32} = \frac{[C_2Cl_4][H^+]^2[Cl^-]^2}{[C_2Cl_6]P_{H_2}}$$

Reductive dechlorination of C_2Cl_6

Using $[H^+] = 10^{-7}$ M & $[Cl^-] = 10^{-3}$ M:

$$\frac{[C_2Cl_4]}{[C_2Cl_6]} = (1.4 \times 10^{52}) \times P_{H_2}$$

- For any reasonable partial pressure of H_2, the amount of C_2Cl_6 remaining at equilibrium is infinitesimal → Thermodynamically the reaction goes all the way to the right

- This reaction mostly occurs biologically, so the presence of microorganisms capable of transforming C_2Cl_6 is required!
  - Organic compound is used as an e- acceptor in this case
  - Note C_2Cl_6 is an anthropogenic compounds → only a limited number of species can use it!