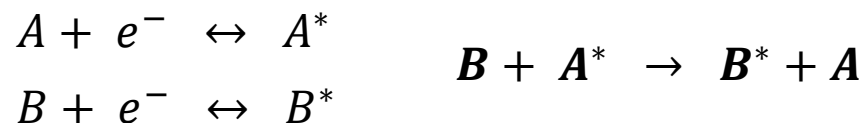


Redox reactions I:

Overview

Oxidation/reduction (redox) reactions

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



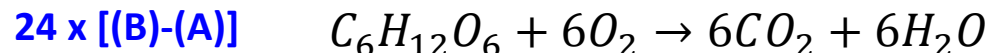
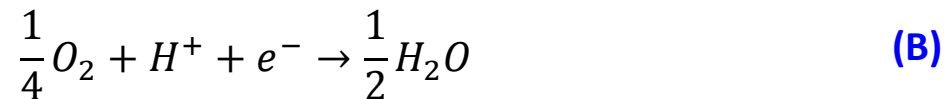
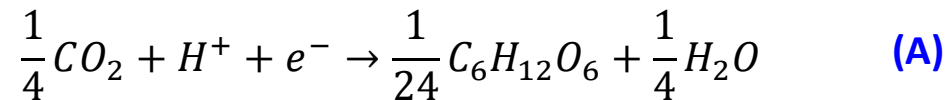
- **Most natural organic compounds are electron donors**

Types of redox reactions (1)

- **Biotic redox reactions**

- Mediated by living organisms
- Redox reactions are the most important type of biotic reactions
- Primary energy source
 - Cell maintenance
 - Cell growth

ex) glucose oxidation mediated by microorganisms



Types of redox reactions (2)

- **Photochemical reactions**
 - Will discuss later
- **Abiotic reactions occurring in the absence of light**
 - May involve mediators/catalysts
 - Although the reaction itself is abiotic, biological molecules can be involved

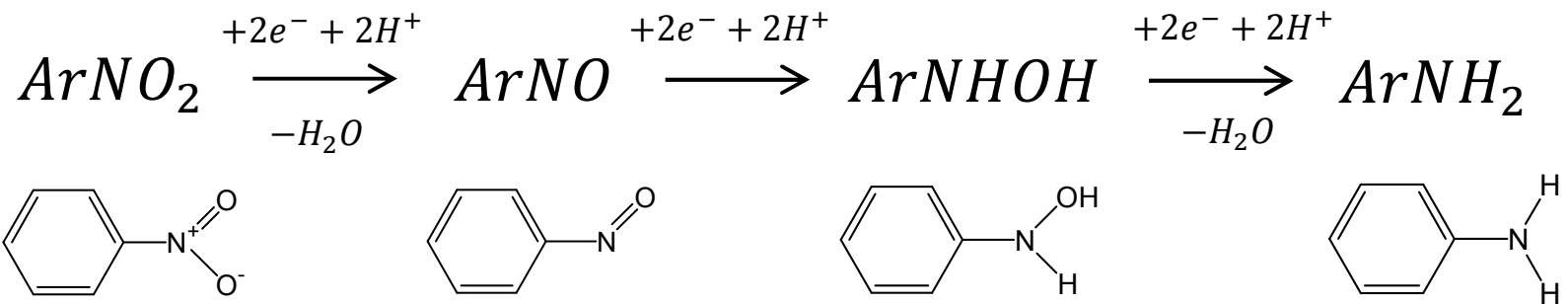
Some selected half reactions

Oxidized species		Reduced species
$\frac{1}{4}O_2 + H^+ + e^-$	=	$\frac{1}{2}H_2O$
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	=	$\frac{1}{10}N_2 + \frac{3}{5}H_2O$
$\frac{1}{2}MnO_2 + HCO_3^- + \frac{3}{2}H^+ + e^-$	=	$\frac{1}{2}MnCO_3 + H_2O$
$\frac{1}{2}NO_3^- + H^+ + e^-$	=	$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O$
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	=	$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$
$\frac{1}{2}CH_3COCOO^-$ (pyruvate) + $H^+ + e^-$	=	$\frac{1}{2}CH_3CHOHCOO^-$ (lactate)
$\frac{1}{8}CO_2 + H^+ + e^-$	=	$\frac{1}{8}CH_4 + \frac{1}{4}H_2O$
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^-$	=	$\frac{1}{8}HS^- + \frac{1}{2}H_2O$
$\frac{1}{2}S + H^+ + e^-$	=	H_2S
$H^+ + e^-$	=	$\frac{1}{2}H_2$
$\frac{1}{4}CO_2 + H^+ + e^-$	=	$\frac{1}{24}C_6H_{12}O_6$ (glucose) + $\frac{1}{4}H_2O$

Abiotic redox reaction example

- 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



oxidation
state:

N()

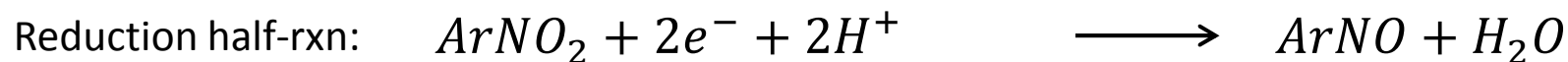
N()

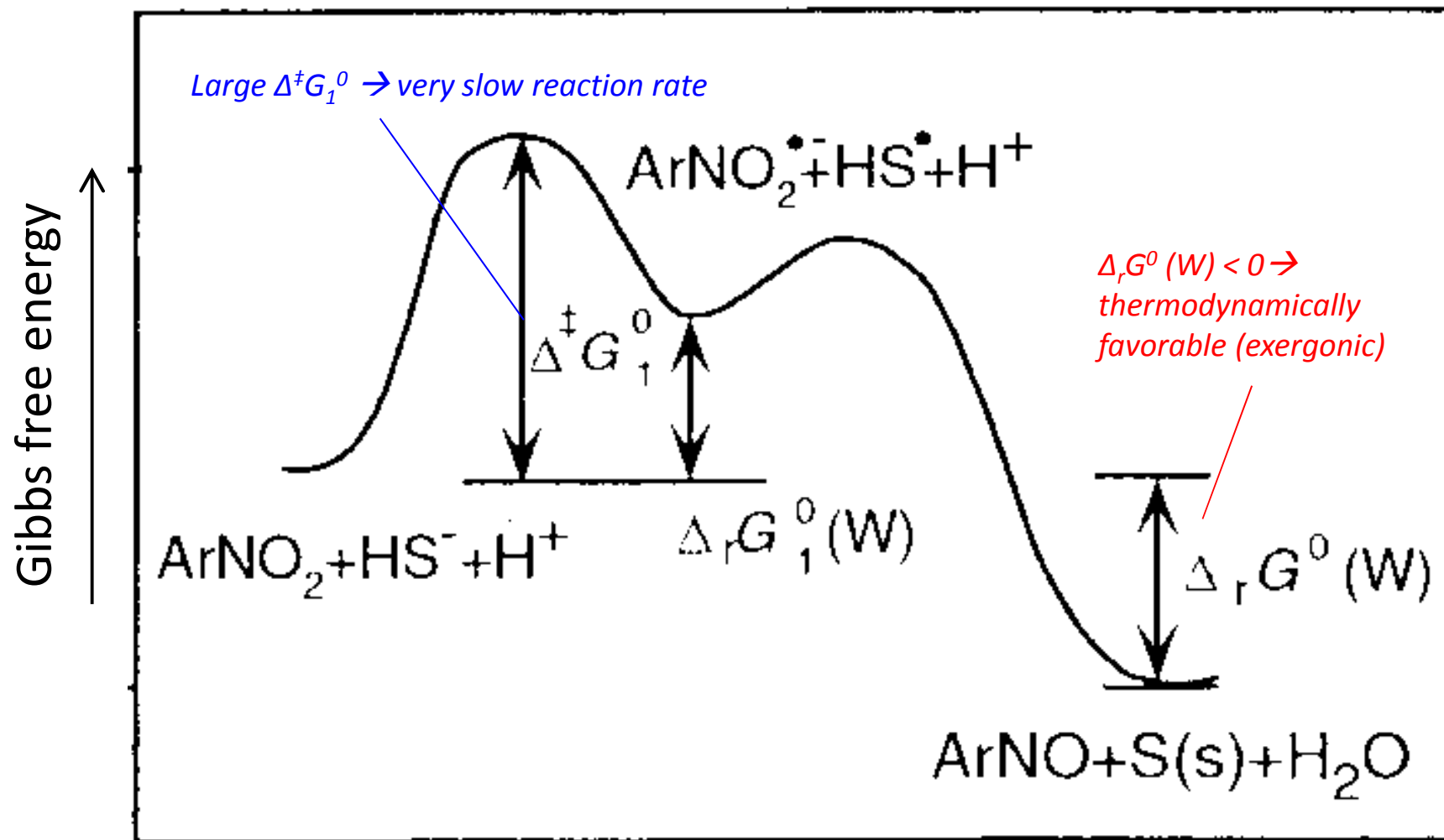
N()

N()

* Ar denotes C_6H_5

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

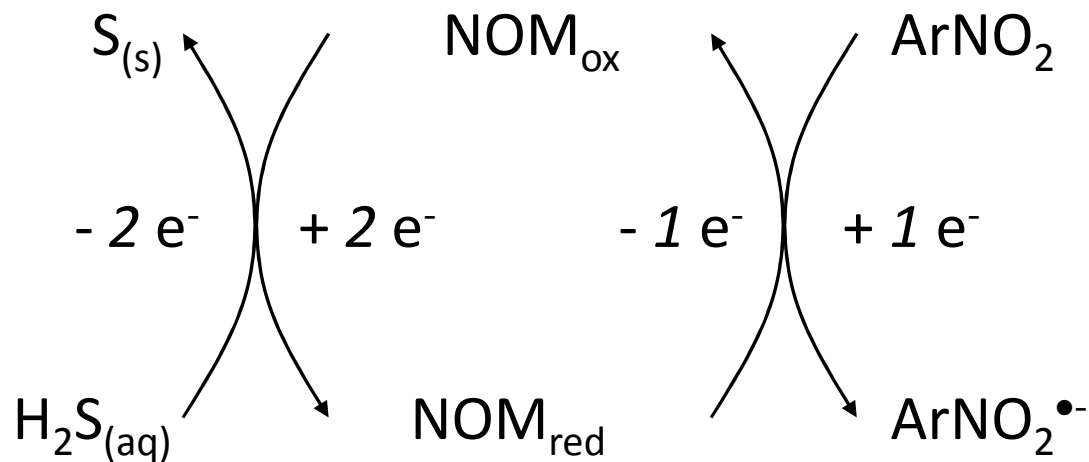




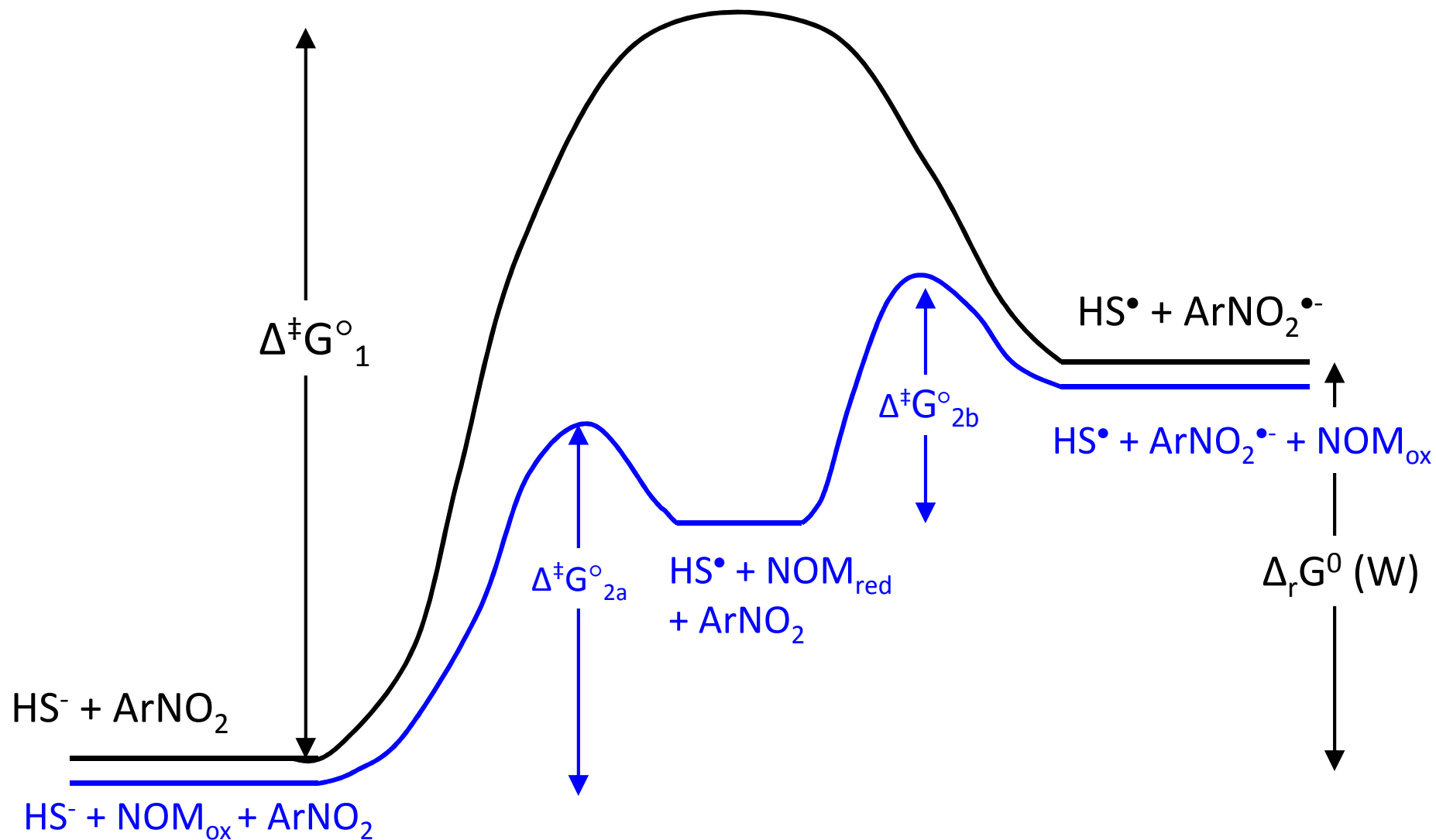
#1

Mediation of redox reaction by NOM

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



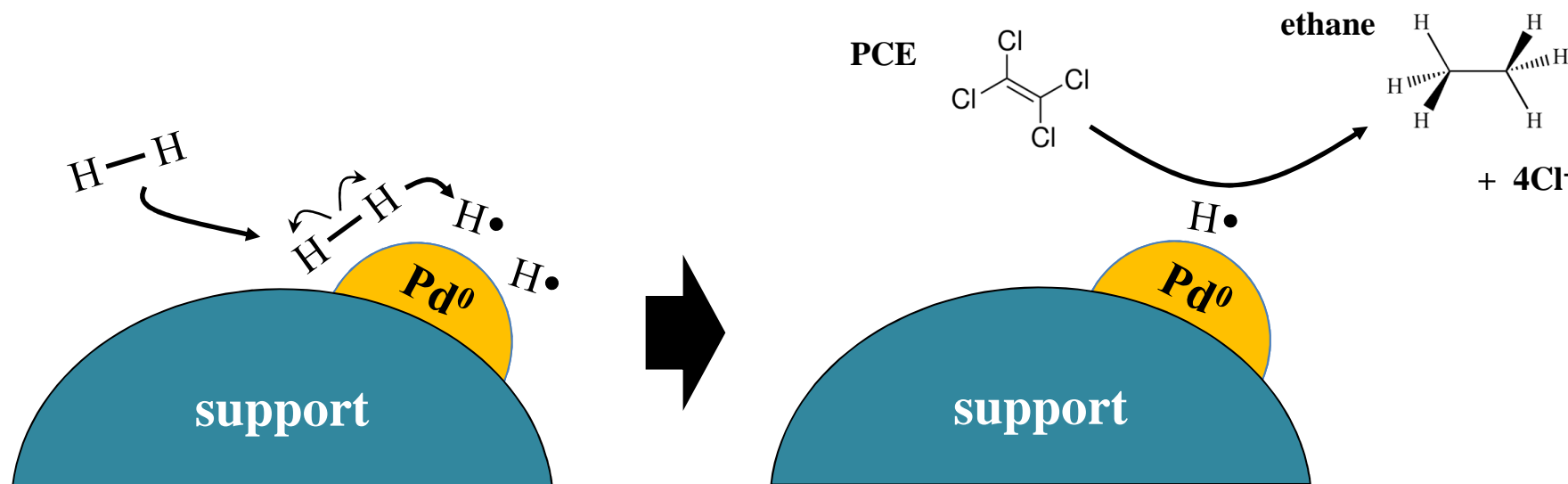
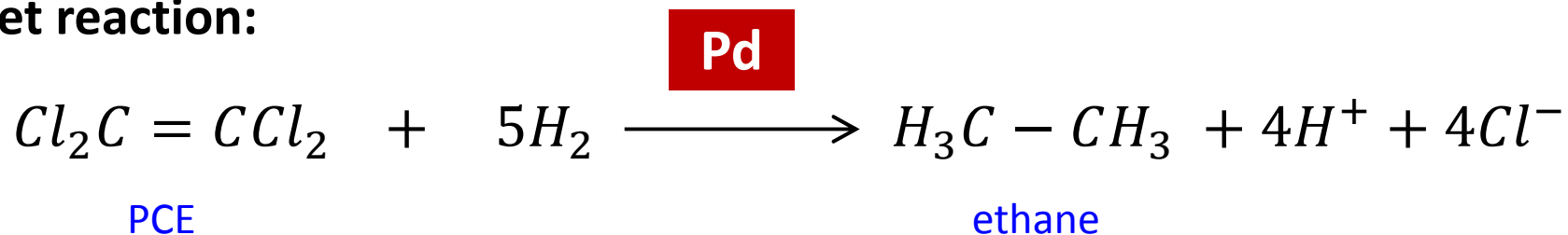
- So ultimately electrons flow from H_2S to $ArNO_2$



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

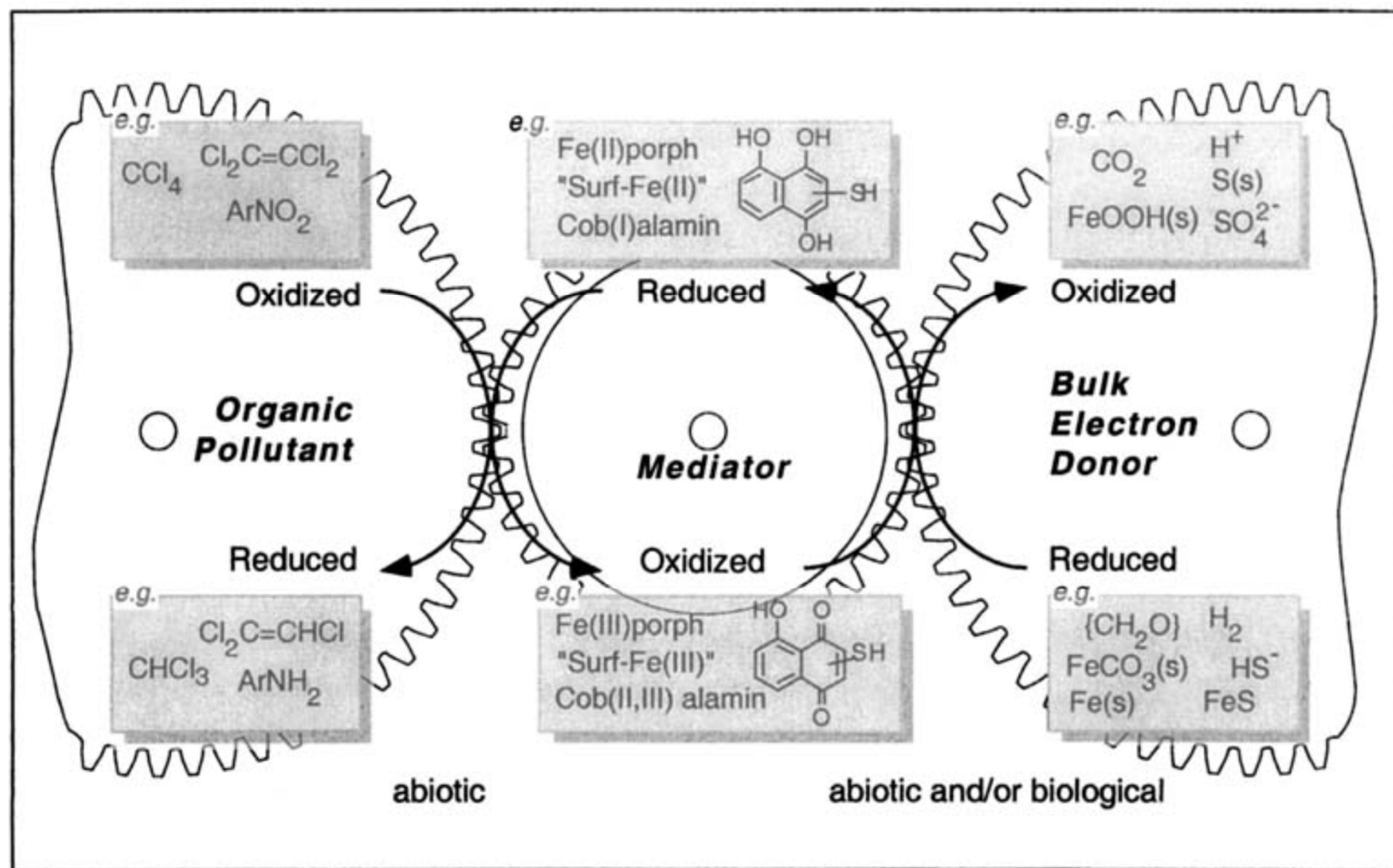
ex2) Pd-catalyzed hydrodehalogenation

Net reaction:



- Pd dissociates H₂ molecules
- Rapid reduction of TCE at the surface of Pd

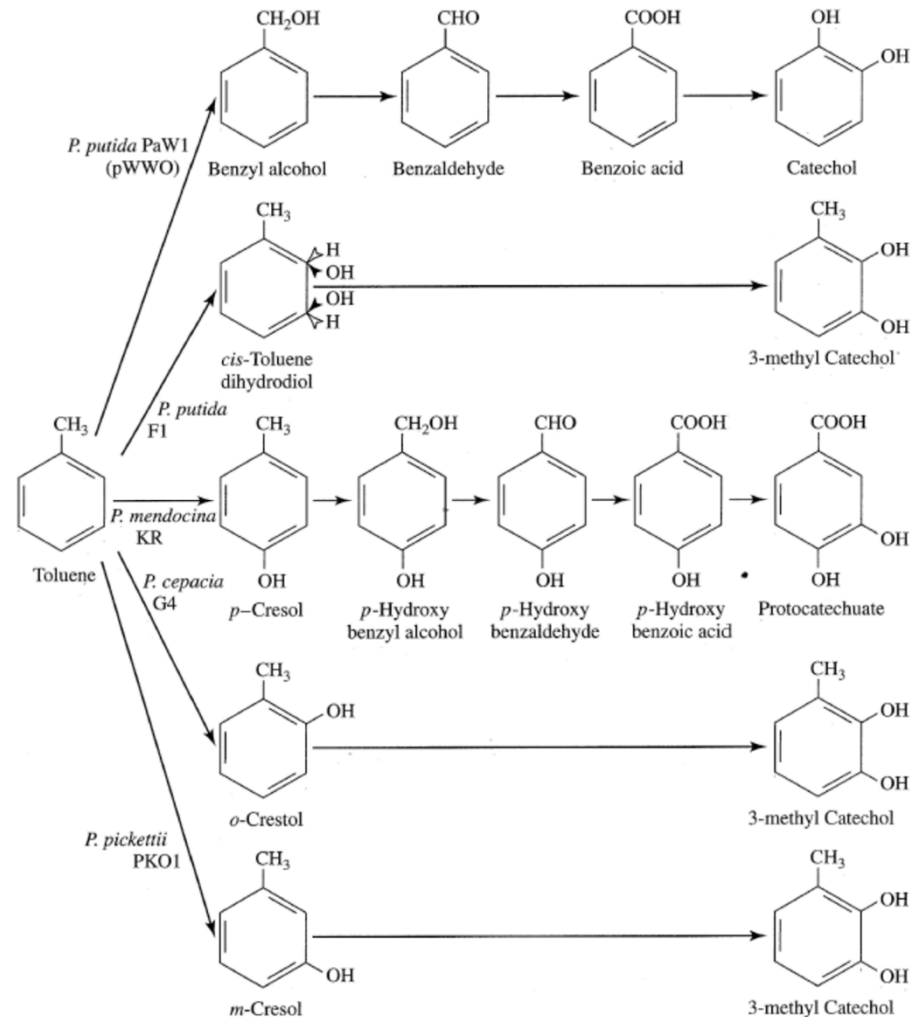
ex3) Redox rxn mediated by biomolecules



Multiple pathways of redox reaction, ex1

- **Aerobic microbial transformation of toluene**

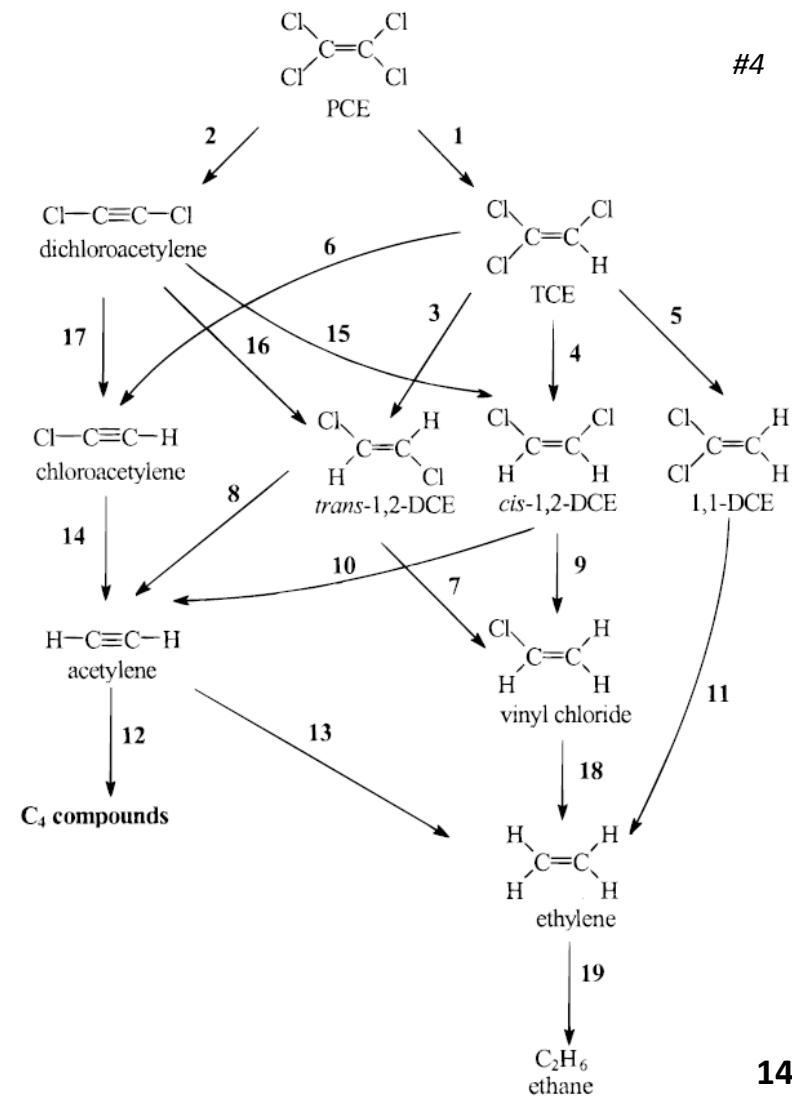
Five different aerobic biodegradation pathways for toluene, each initiated through the activity of a mono- or dioxygenase together with molecular oxygen.



Multiple pathways of redox reaction, ex2

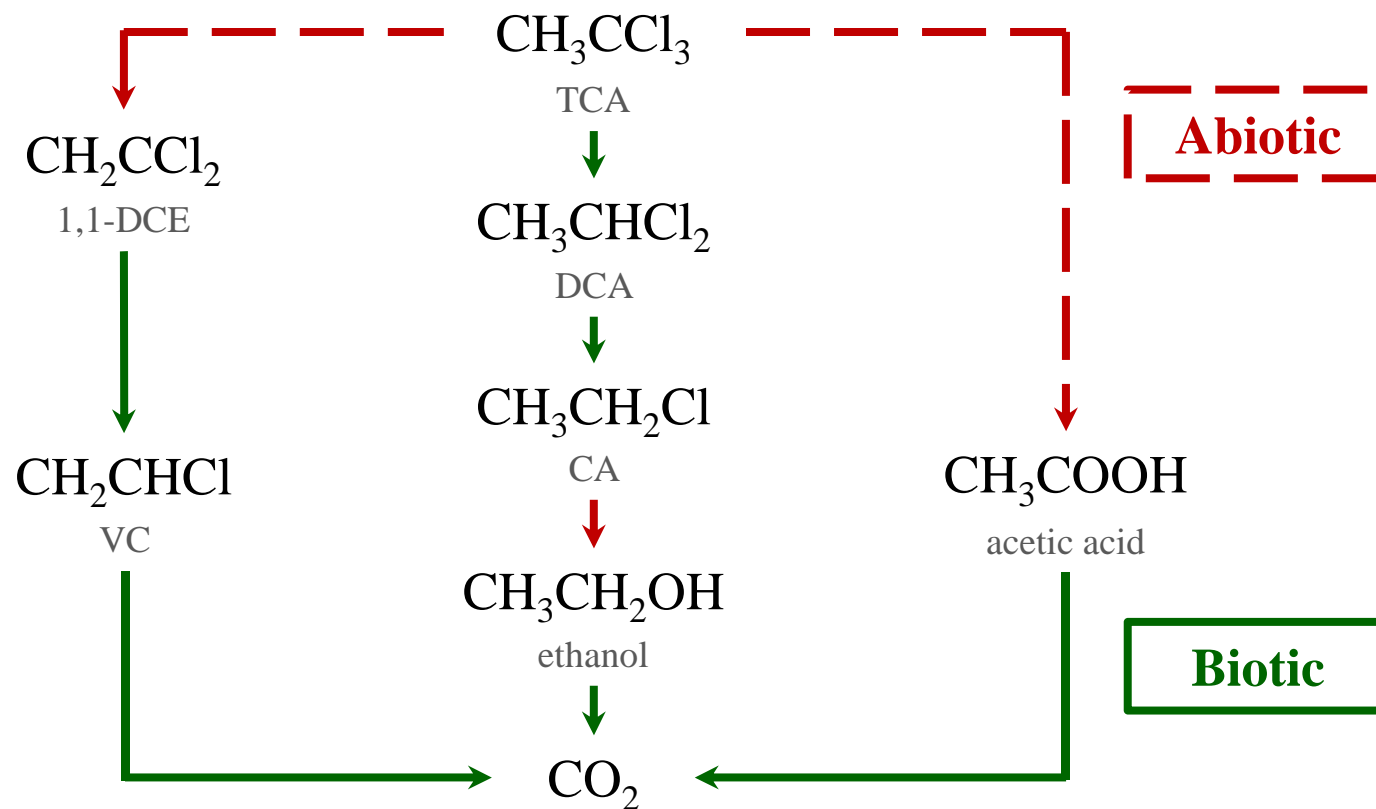
- Anaerobic PCE reaction pathways with zero valent iron (Fe^0) (abiotic)

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



Multiple pathways of redox reaction, ex3

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



#5, adapted

References

- #1, #2) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, p. 586; p. 557.
- #3) Mikesell, M. D., Kukor, J. J., Olsen, R. H. (1993) Metabolic diversity of aromatic hydrocarbon-degrading bacteria from a petroleum-contaminated aquifer. *Biodegradation*, 4, 249-259.
- #4) Arnold, W. A., Roberts, A. L. (2000) Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environmental Science & Technology*, 34, 1794-1805.
- #5) Vogel, T. M., McCarty, P. L. (1987) Abiotic and biotic transformations of 1,1,1-trichloroethane under methanogenic conditions. *Environmental Science & Technology*, 21, 1208-1213.

Redox reactions II:

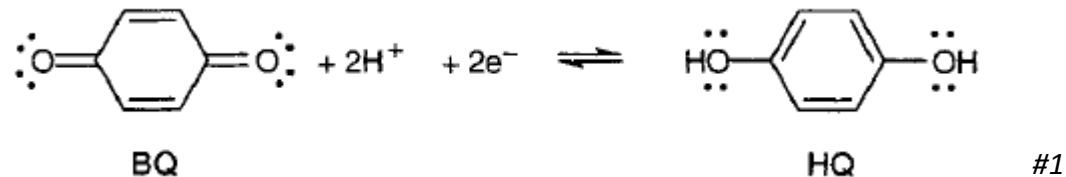
Fundamentals of thermodynamics

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 $\Delta G_{r(\text{reduction})}$ & $\Delta G_{r(\text{oxidation})}$ to obtain $\Delta G_{r(\text{overall})}$
- **How do we determine ΔG_r of half reactions by experiments?**

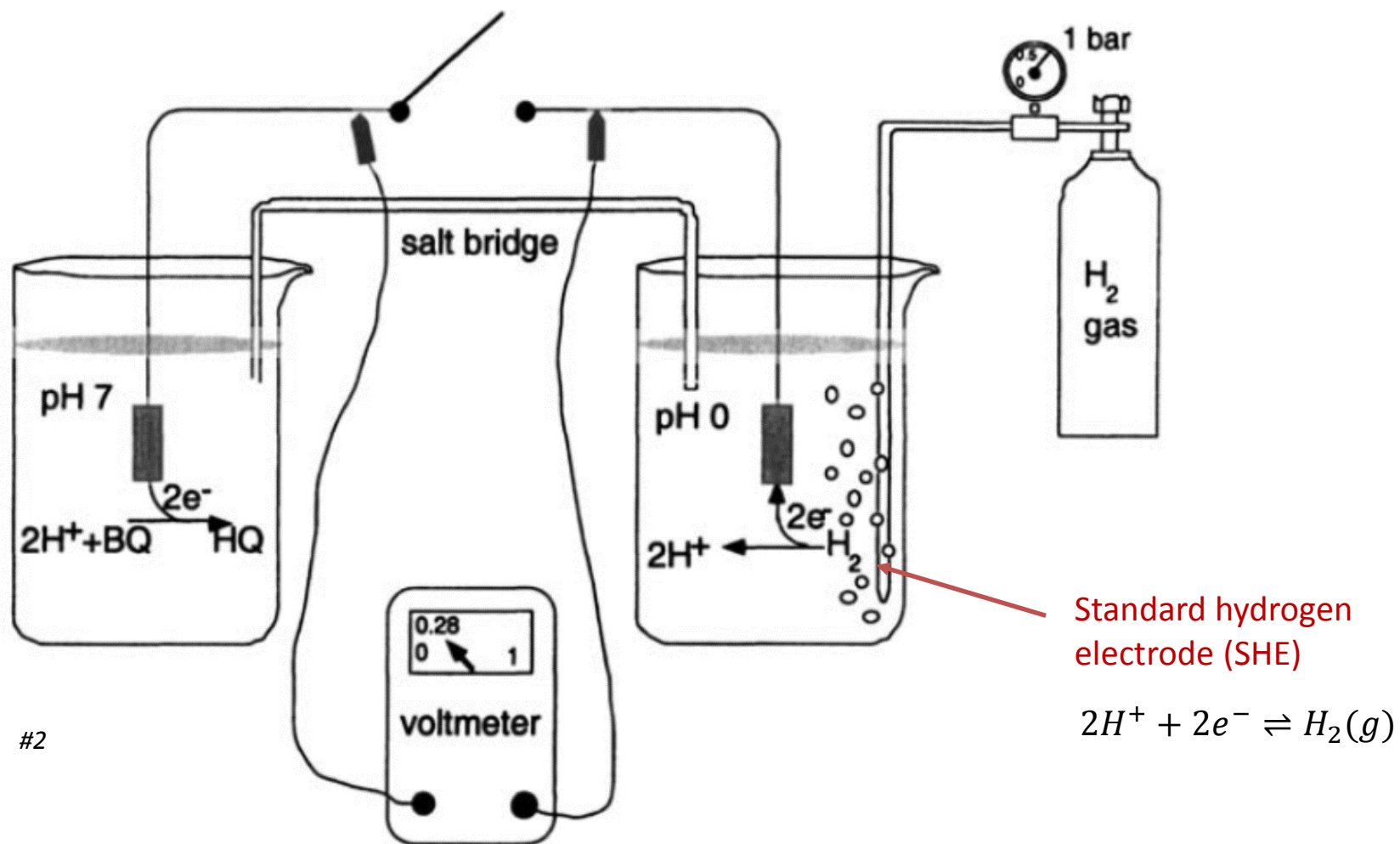
Determining ΔG_r of half reactions

- 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 ($p_{H_2} = 1 \text{ bar}$) – standard hydrogen electrode (SHE)

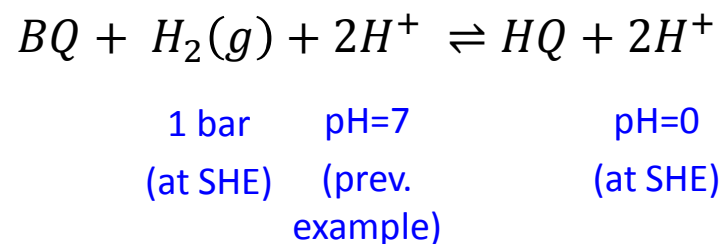
Experimental setting



#2

Reactions involved

- **Overall reaction:**



- **With half reactions:**



ΔE (electrical potential) & ΔG_r (free E)

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:

$$\Delta_r G = -nF\Delta E$$

n = number of electrons transferred

F = Faraday constant, 96485 Coulomb/mol

= 96.5 kJ/mol-V

E_H & E_H^0

- The electrical potential relative to SHE, E_H

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

- 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

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

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

Nernst equation

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 $aA + bB = cC + dD$,

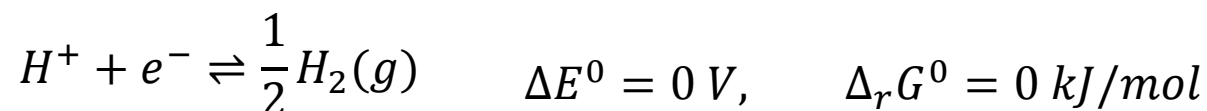
$$Q_r = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

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
 - $[Cl^-] = 10^{-3} \text{ M}$; $[Br^-] = 10^{-5} \text{ M}$
 - Organic oxidant and reductant have unit activities

At the SHE...

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



- Standard conditions are met at the SHE: $\{H^+\} = 1$, $P_{H_2} = 1 \text{ bar}$
- Check Q_r for the overall reaction and the half reaction at BQ-HQ electrode:



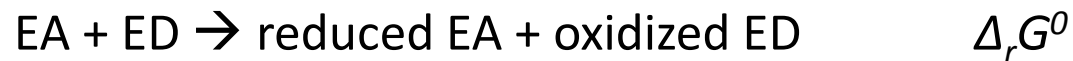
$$Q_r(\text{overall rxn}) = \frac{\{HQ\}\{H^+\}_{SHE}^2}{\{BQ\}P_{H_2}\{H^+\}_{BQ-HQ}^2} = \frac{\{HQ\}}{\{BQ\}\{H^+\}_{BQ-HQ}^2} = Q_r(\text{half rxn})$$



- Therefore, the electrical potential change of the BQ-HG half reaction can be directly measured by the electrical potential change at the galvanic cell

Thermodynamics of redox reactions - recap

- The overall free energy change of a redox reaction:



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

- Under the standard conditions:

- Negative Δ_rG^0 : favorable reaction
- Large $|\Delta_rG^0|$ (*with* $\Delta_rG^0 < 0$): strong driving force for the forward reaction, makes the backward reaction difficult
- Note: this is thermodynamics, **NOT** kinetics!

References

#1, #2) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, p. 561; p. 560.

Redox reactions III:

Application of thermodynamics

Applying thermodynamics – simple example

	$\Delta G^0(W)/e^-, \text{ kJ/mol}$
A $2H^+ + 2e^- \leftrightarrow H_2 (g)$	+40.0
B $O_2 (g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	-78.3
B-2A $2H_2 (g) + O_2 (g) \leftrightarrow 2H_2O$	

$$\begin{aligned}\Delta_r G^0 &= 4 \times (-78.3 - 40.0) \\ &= -473.2 \text{ kJ/mol } O_2\end{aligned}$$

The equilibrium constant for this reversible reaction:

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

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

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

➡ $\Delta_r G^0 = -RT \ln(K)$

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

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

Half reactions - expanded

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

#1

Halfreaction		E_H^0 (V)	$E_H^0(W)$ (V)	$\Delta_r G^0(W)/n^c$ (kJ·mol ⁻¹)
Oxidized Species	Reduced Species			
(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 ₃ CHOHCOO ⁻ (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) $6 CO_2(g) + 24 H^+ + 24 e^- = C_6H_{12}O_6(\text{glucose}) + 6 H_2O$		-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

#2

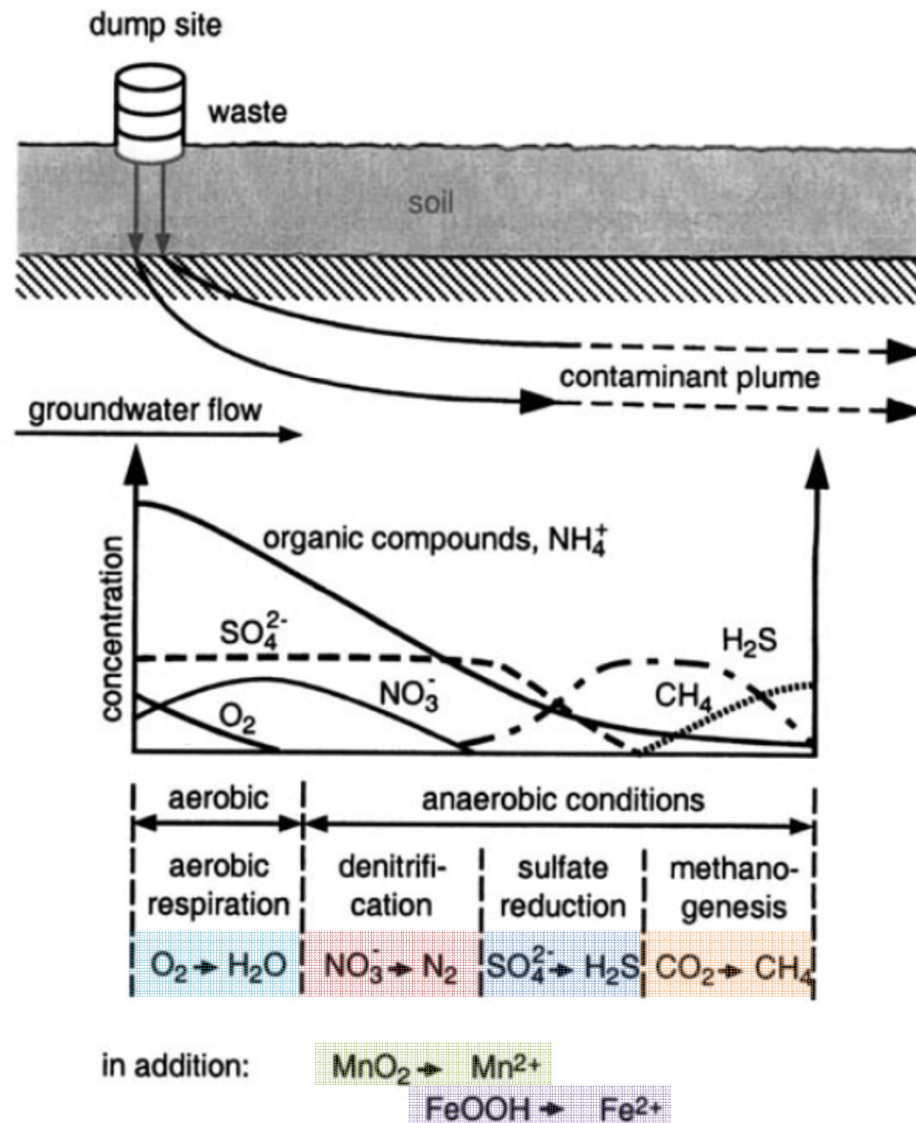



Figure 14.3 Variation in concentrations of important dissolved redox species along the flowpath of a contaminant plume in groundwater. This sequence results in several zones of characteristic microbial metabolism and corresponding redox conditions (adapted from Bouwer et al., 1984).

Oxidation cascade – why?

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

- 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

Redox reaction of organohalogenes

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

#3

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)	
(1)	$\text{CCl}_3-\text{CCl}_3 + 2e^-$	=	$\text{Cl}_2\text{C}=\text{CCl}_2 + 2\text{Cl}^-$	+ 0.95	+ 1.13	- 109.0
(2)	$\text{CBr}_4 + \text{H}^+ + 2e^-$	=	$\text{CHBr}_3 + \text{Br}^-$	+ 0.89	+ 0.83	- 80.1
(3)	$\text{CCl}_4 + \text{H}^+ + 2e^-$	=	$\text{CHCl}_3 + \text{Cl}^-$	+ 0.79	+ 0.67	- 64.7
(4)	$\text{CHBr}_3 + \text{H}^+ + 2e^-$	=	$\text{CH}_2\text{Br}_2 + \text{Br}^-$	+ 0.67	+ 0.61	- 58.9
(5)	$\text{Cl}_2\text{C}=\text{CCl}_2 + \text{H}^+ + 2e^-$	=	$\text{Cl}_2\text{C}=\text{CHCl} + \text{Cl}^-$	+ 0.70	+ 0.58	- 56.0
(6)	$\text{CHCl}_3 + \text{H}^+ + 2e^-$	=	$\text{CH}_2\text{Cl}_2 + \text{Cl}^-$	+ 0.68	+ 0.56	- 54.0
(7)	+ $\text{H}^+ + 2e^-$	=	+ Cl^-	+ 0.68	+ 0.56	- 54.0
(8)	+ $\text{H}^+ + 2e^-$	=	+ Cl^-	+ 0.54	+ 0.42	- 40.5

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

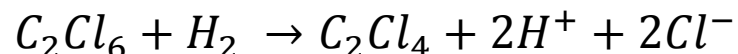
Reductive dechlorination of C_2Cl_6

	E_H^0, V	$\Delta_r G^0, kJ/mol$ $= -nFE_H^0$
<i>Eq. (1) of Table 14.3:</i>		
$C_2Cl_6 + 2e^- \rightarrow C_2Cl_4 + 2Cl^-$	0.95	-183.4

Couple with Eq. 11b of Table 14.2:

$2H^+ + 2e^- \rightarrow H_2$	0	0
-------------------------------	---	---

Overall reaction:



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

$$\Delta_r G^0 = -RT \ln K$$

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

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

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

- For any reasonable partial pressure of H_2 , the amount of C_2Cl_6 remaining at equilibrium is infinitesimal \rightarrow 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 \rightarrow only a limited number of species can use it!

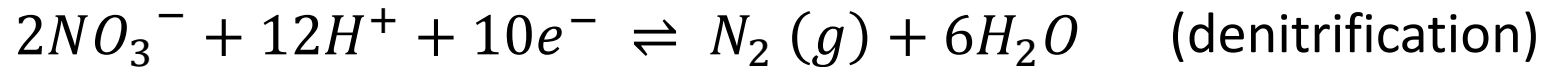
References

#1, #2, #3) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, p. 563; p. 570; p. 564.

Redox reactions: Exercise

Rxn free energy & electrical potential

Q: Consider the half reaction in an aqueous solution:



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

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

Rxn free energy & electrical potential

$$E_H^0 = -\frac{\Delta_r G^0}{nF} = -\frac{-1200 \text{ kJ/mol}}{(10) \cdot (96.5 \text{ kJ/mol-V})} = \mathbf{1.24 \text{ V}}$$

$$E_H^0(W) = E_H^0 - \frac{2.303RT}{nF} \log Q_r = 1.24 \text{ V} - \frac{0.059 \text{ V}}{10} \log \left[\frac{\{H_2O\}^6 P_{N_2}}{\{NO_3^-\}^2 \{H^+\}^{12}} \right]$$

pH = 7, other species have unit activity

$$R = 8.314 \times 10^{-3} \text{ kJ/K-mol}$$

$$F = 96.5 \text{ kJ/mol-V}$$

$$= 1.24 \text{ V} - \frac{0.059 \text{ V}}{10} \log \left[\frac{1}{(10^{-7})^{12}} \right] = \mathbf{0.74 \text{ V}}$$

$$\Delta_r G^0(W) = -nFE_H^0(W) = -(10) \cdot \left(96.5 \frac{\text{kJ}}{\text{mole}} - V \right) \cdot (0.74 \text{ V}) = \mathbf{-714 \text{ kJ/mol}}$$

Application of thermodynamics

Q: Determine the hydrogen partial pressure of an air bubble at thermodynamic equilibrium with water having a pH of 8.0 and at a temperature of 25 °C. The oxygen partial pressure of the air bubble is 0.21 atm. Use the following half reactions.



Application of thermodynamics

Overall reaction:



$$\begin{aligned} E_H &= E_H^0 - \frac{2.303RT}{nF} \log Q_r = 1.23 \text{ V} - \frac{0.059 \text{ V}}{4} \log Q_r \\ &= 1.23 \text{ V} - \frac{0.059 \text{ V}}{4} \log \left[\frac{1}{P_{O_2} P_{H_2}^2} \right] \end{aligned}$$

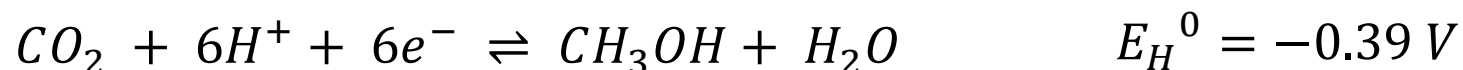
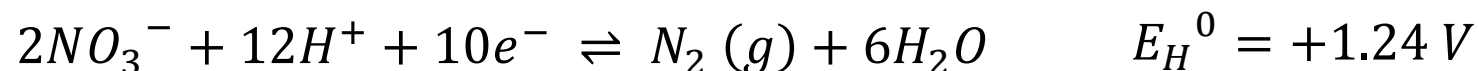
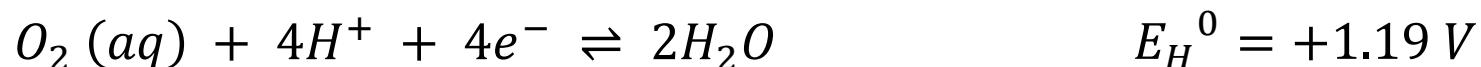
For thermodynamic equilibrium, E_H should be zero.

$$Q_r = \frac{1}{P_{O_2} P_{H_2}^2} = 10^{1.23/(0.059/4)} = 2.45 \times 10^{-83}$$

$$P_{H_2} = \{(2.45 \times 10^{-83}) \cdot 0.21\}^{1/2} = \mathbf{2.27 \times 10^{-42} \text{ atm}}$$

Comparing thermodynamic favorability

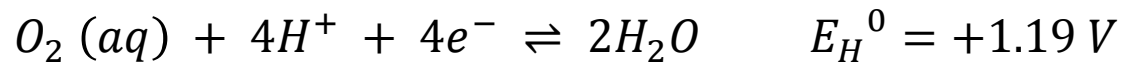
Q: A synthetic wastewater sample is prepared by adding 1 mM methanol and 1 mM sodium nitrate (NaNO_3) in pure water. The dissolved oxygen (DO) concentration in the sample is maintained at 8 mg/L the pH at 7.0, and the temperature at 25 °C. Bacteria capable of mineralizing methanol using either oxygen or nitrate as an electron acceptor is inoculated into the wastewater. Considering the thermodynamics, which one will be the preferred electron acceptor? Assume a nitrogen partial pressure of 0.78 atm. If needed, use the following half reactions.



Comparing thermodynamic favorability

For comparison of the favorability of the electron acceptors, analyzing the electron acceptor half reactions is sufficient. CO₂-methanol half reaction is not necessary.

Calculate the E_H values of the electron acceptor half reactions using the conditions given:

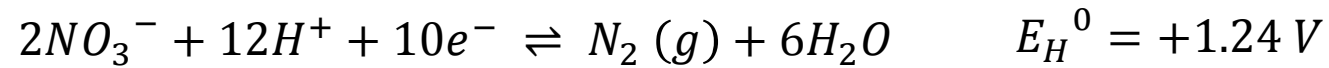


$$E_H = E_H^0 - \frac{2.303RT}{nF} \log Q_r = 1.23 V - \frac{0.059 V}{4} \log \frac{1}{[O_2][H^+]^4}$$

$$[O_2] = \frac{0.008 \text{ g/L}}{32 \text{ g/mol}} = 2.5 \times 10^{-4} M$$

$$E_H = 1.23 V - \frac{0.059 V}{4} \log \frac{1}{(2.5 \times 10^{-4}) \cdot (10^{-7})^4}$$

$$= \mathbf{0.76 V}$$



$$E_H = E_H^0 - \frac{2.303RT}{nF} \log Q_r = 1.24 V - \frac{0.059 V}{10} \log \frac{P_{N_2}}{[NO_3^-]^2 [H^+]^{12}}$$

$$= 1.24 V - \frac{0.059 V}{10} \log \frac{0.78}{(10^{-3})^2 \cdot (10^{-7})^{12}}$$

$$= 0.71 V$$

→ Oxygen is the preferred electron acceptor.