Redox reactions III: Application of thermodynamics

Applying thermodynamics – simple example

		ΔG⁰(W)/e ⁻, kJ/mol
Α	$2H^{+} + 2e^{-} \leftrightarrow H_{2}(g)$	+40.0
В	$O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	-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:

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

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

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 $E_{\rm H}^0(W)$ values.)^{*a*}

	Halfreaction	_		
	Oxidized Species Reduced Species	$E_{\rm H}^0$ (V)	$E_{\rm H}^0({ m W})$ (V)	$\Delta_{\rm r}G^0({\rm W})/n^c$ (kJ·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)	$HCO_{3} + 9 H^{+} + 8 e^{-} = CH_{4}(aq) + 3 H_{2}O$	+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)	$6 \text{ CO}_2(g) + 24 \text{ H}^+ + 24 \text{ e}^- = \text{C}_6\text{H}_{12}\text{O}_6(\text{glucose}) + 6 \text{ H}_2\text{O}$	-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 $[HCO_{\frac{1}{3}}] = 10^{-3}$ M.

c n = number of electrons transferred.

Oxidation cascade



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?

	⊿ _r G⁰(W) (kJ/mol glucose
$C_6H_{12}O_6 + \frac{6O_2}{6} \Rightarrow 6CO_2 + 6H_2O$	-2863.2
$C_6H_{12}O_6 + \frac{4.8NO_3}{1} + 4.8H^+ \Rightarrow 6CO_2 + 2.4N_2 + 8.4H_2O$	-2714.4
$C_6H_{12}O_6 + 24FeOOH(s) + 24HCO_3^- + 24H^+$	-868.8
$\Rightarrow \ 6CO_2 + 24FeCO_3 + 42H_2O$	
$C_6H_{12}O_6 + 3SO_4^{2-} + 3H^+ \Rightarrow 6CO_2 + 3HS^- + 6H_2O$	-482.4
$C_6 H_{12} O_6 \Rightarrow 3CO_2 + 3CH_4$	-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 6

Redox reaction of organohalogens

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 $E_{\rm H}$ (W) values.)^{*a*}

Halfreaction						
Oxidized Species		F	Reduced Species		E _H ⁰ (W) ^b (V)	$\Delta_r G^0(W)/n^c$ (kJ·mol ^{-l})
(1)	CCI ₃ CCI ₃ + 2 e.	=	Cl ₂ C=CCl ₂ + 2Cl	+ 0.95	+ 1.13	- 109.0
(2)	CBr ₄ + H ⁺ + 2e ⁻	-	CHBr ₃ + Br	+ 0.89	+ 0.83	- 80.1
(3)	CCI4 + H+ + 2e-	=	CHCI3+CI	+ 0.79	+ 0.67	- 64.7
(4)	CHBr _a + H* + 2e ⁻	-	CH ₂ Br ₂ + Br	+ 0.67	+ 0.61	- 58.9
(5)	Cl ₂ C=CCl ₂ + H+ + 2e ⁻	-	Cl ₂ C=CHCl + Cl	+ 0.70	+ 0.58	- 56.0
(6)	CHCl ₃ + H* + 2e ⁻	=	CH ₂ Cl ₂ + Cl ²	+ 0.68	+ 0.56	- 54.0
(7)	Cl ₆ + H+ + 2e-	-	CI ₅ + CI ⁺	+ 0.68	+ 0.56	- 54.0
(8)	Ct + H* + 26.	-	- CF	+ 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*} [H⁺] = 10⁻⁷, {CI⁻} = 10⁻³, {Br⁻} = 10⁻⁵. ^{*c*} n = number of electrons transferred.

Reductive dechlorination of C₂Cl₆

Eq. (1) of Table 14.3:	E _H ⁰ , V	∆_rG⁰ , kJ/mol =-nFE _H ⁰
$C_2Cl_6 + 2e^- \rightarrow C_2Cl_4 + 2Cl^-$	0.95	-183.4
Couple with Eq. 11b of Table 14.2:		
$2H^+ + 2e^- \rightarrow H_2$	0	0

Overall reaction:

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

 $\Delta_r G^0 = -183.4 - 0 = -183.4 \, kJ/mol \, C_2 C l_6$

 $\Delta_r G^0 = -RT lnK$

$$K = e^{-\Delta_r G^0/RT} = 1.4 \times 10^{32} = \frac{[C_2 C l_4][H^+]^2 [C l^-]^2}{[C_2 C l_6] P_{H_2}}$$

Using
$$[H^+] = 10^{-7} M \& [Cl^-] = 10^{-3} M$$
:
$$\frac{[C_2 C l_4]}{[C_2 C l_6]} = (1.4 \times 10^{52}) \times P_{H_2}$$

- For any reasonable partial pressure of H₂, the amount of C₂Cl₆ 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 C₂Cl₆ 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!

Redox reactions: Exercise

Rxn free energy & electrical potential

Q: Consider the half reaction in an aqueous solution:

 $2NO_3^- + 12H^+ + 10e^- \rightleftharpoons N_2(g) + 6H_2O$ (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.

Solution)

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

$$E_{H}^{0}(W) = E_{H}^{0} - \frac{2.303RT}{nF} \log Q_{r} = 1.24 V - \frac{0.059 V}{10} \log \left[\frac{\{H_{2}O\}^{6} P_{N_{2}}}{\{NO_{3}^{-}\}^{2} \{H^{+}\}^{12}} \right]$$

$$pH = 7, other species have unit activity$$
$$= 1.24 V - \frac{0.059 V}{10} log \left[\frac{1}{(10^{-7})^{12}}\right] = 0.74 V$$

R = 8.314 x 10⁻³ kJ/K-mol F = 96.5 kJ/mol-V

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

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.

$$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$
 $E_H^{0} = +1.23 V$
 $2H^+ + 2e^- \rightleftharpoons H_2(g)$ $E_H^{0} = 0.00 V$

Solution)

Overall reaction:

 $2H_{2}(g) + O_{2}(g) \rightleftharpoons 2H_{2}O \qquad E_{H}^{0} = +1.23 - 0.00 = +1.23 V$ $E_{H} = E_{H}^{0} - \frac{2.303RT}{nF} \log Q_{r} = 1.23 V - \frac{0.059 V}{4} \log Q_{r}$ $= 1.23 V - \frac{0.059 V}{4} \log \left[\frac{1}{P_{O_{2}}P_{H_{2}}^{2}}\right]$

For thermodynamic equilibrium, E_H should be zero.

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

 $P_{H_2} = \{(2.45 \times 10^{-83}) \cdot 0.21\}^{1/2} = \mathbf{2} \cdot \mathbf{27} \times \mathbf{10^{-42}} atm$

Comparing thermodynamic favorability

Q: A synthetic wastewater sample is prepared by adding 1 mM methanol and 1 mM sodium nitrate (NaNO₃) 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.

$$O_{2}(aq) + 4H^{+} + 4e^{-} \rightleftharpoons 2H_{2}O \qquad E_{H}^{0} = +1.19V$$

$$2NO_{3}^{-} + 12H^{+} + 10e^{-} \rightleftharpoons N_{2}(g) + 6H_{2}O \qquad E_{H}^{0} = +1.24V$$

$$CO_{2} + 6H^{+} + 6e^{-} \rightleftharpoons CH_{3}OH + H_{2}O \qquad E_{H}^{0} = -0.39V$$

Solution)

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:

 $O_{2}(aq) + 4H^{+} + 4e^{-} \rightleftharpoons 2H_{2}O \qquad E_{H}^{0} = +1.19V$ $E_{H} = E_{H}^{0} - \frac{2.303RT}{nF} \log Q_{r} = 1.23V - \frac{0.059V}{4} \log \frac{1}{[O_{2}][H^{+}]^{4}}$ $[O_{2}] = \frac{0.008 g/L}{32 g/mol} = 2.5 \times 10^{-4} M$

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

= 0.76 V

$$2NO_3^- + 12H^+ + 10e^- \rightleftharpoons N_2(g) + 6H_2O \qquad E_H^0 = +1.24V$$

$$E_{H} = E_{H}^{0} - \frac{2.303RT}{nF} \log Q_{r} = 1.24 V - \frac{0.059 V}{10} \log \frac{P_{N_{2}}}{[NO_{3}^{-}]^{2}[H^{+}]^{12}}$$
$$= 1.24 V - \frac{0.059 V}{10} \log \frac{0.78}{(10^{-3})^{2} \cdot (10^{-7})^{12}}$$
$$= 0.71 V$$

\rightarrow Oxygen is the preferred electron acceptor.

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 $\Delta G_{r (reduction)} \& \Delta G_{r (oxidation)}$ to obtain $\Delta G_{r (overall)}$
- 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



Reactions involved

• Overall reaction:

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

1 bar	рн=7	рн=о
(at SHE)	(prev.	(at SHE)
	example)	

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

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



• 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

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

$$E_{H} = E_{H}^{0} - \frac{RT}{nF} lnQ_{r} = E_{H}^{0} - \frac{2.303RT}{nF} logQ_{r}$$
 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_H⁰*
 - All reaction components have unit activities
- E_H⁰ (W)
 - *E_H* under **<u>typical natural water conditions</u>**:
 - pH = 7
 - [Cl⁻] = 10⁻³ M; [Br⁻] = 10⁻⁵ 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:

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

- Standard conditions are met at the SHE: $\{H^+\} = 1$, $P_{H_2} = 1$ bar
- Check Q_r for the overall reaction and the half reaction at BQ-HQ electrode: $BQ + H_2(g) + 2H^+ \rightleftharpoons HQ + 2H^+$ $Q_r(overall rxn) = \frac{\{HQ\}\{H^+\}_{SHE}^2}{\{BQ\}P_{H_2}\{H^+\}_{BQ-HQ}^2} = \frac{\{HQ\}}{\{BQ\}\{H^+\}_{BQ-HQ}^2} = Q_r(half rxn)$ BQ-HQ half reaction: $BQ + 2H^+ + 2e^- \rightleftharpoons HQ$
- 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:

Reduction: EA + $e^- \rightarrow$ reduced EA $\Delta_{red}G^0$ Oxidation: ED \rightarrow oxidized ED + $e^ \Delta_{oxi}G^0$

 $EA + ED \rightarrow reduced EA + oxidized ED \qquad \Delta_r G^0$ $\Delta_r G^0 = \Delta_{red} G^0 + \Delta_{oxi} G^0$

- 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, **NOT** kinetics!