

Table 15.6-1 Redox Reactions in Chemolithotrophic Bacteria

Reducant	Redox Couple*	E°_{red} [mV]	Reactions	$\Delta G'_{\text{red}} \text{ [kJ}^\circ\text{mol}^{-1}\text{]}^{**}$	Enzymes; Cofactors	Organisms
Carbon monoxide	CO/CO_2	-540	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^-$		carbon monoxide dehydrogenase	'Carboxidobacteria', e.g. <i>Pseudomonas</i>
	$\text{O}_2 (0.21 \text{ atm})/\text{H}_2\text{O}$	+816	$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-261		
Hydrogen	$2 \text{H}/\text{H}_2$	-410	$\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$		hydrogenase, [NiFe] or [Fe]	'Knallgas' bacteria
			$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-237		
Sulfide	S_0/HS^-	-260	$\text{HS}^- \rightarrow \text{S}_0 + \text{H}^+ + 2 \text{e}^-$		'sulfide oxidase'	<i>Thiobacillus</i> ; <i>Beggiatoa</i> ; <i>Wolinella succinogenes</i> (uses fumarate as el. acc.)
			$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{HS}^- + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{S}_0 + \text{H}_2\text{O}$	-207		
	$\text{HSO}_3^-/\text{HSO}_4^-$	-110	$\text{HSO}_3^- + 3 \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + 6 \text{H}^+ + 6 \text{e}^-$		sulfite reductase; siroheme, FeS	<i>Thiobacillus</i> ; <i>Sulfolobus</i>
			$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{HSO}_3^- + \frac{1}{2}\text{O}_2 \rightarrow \text{HSO}_4^-$	-536		
Sulfur	$\text{HSO}_4^-/\text{S}_0$	-45	$\text{S}_0 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{S}_{n+1} + \text{HSO}_4^- + \text{H}^+$	-332	'sulfur dioxygenase'; FeS	<i>Thiobacillus</i>
Sulfite	$\text{SO}_3^{2-}/\text{HSO}_3^-$	-520	$\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + 3 \text{H}^+ + 2 \text{e}^-$		sulfite: cytochrome c oxidoreductase; heme-Fe, Mo ⁺⁺	<i>Thiobacillus</i> (<i>T. denitrificans</i> uses NO_3^- as electron acceptor anaerobically)
			$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{HSO}_3^- + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3^{2-} + \text{H}^+$	-258		
	$\text{APS}/\text{HSO}_3^-$	-60	a) $\text{HSO}_3^- + \text{AMP} \rightarrow \text{APS} + 2 \text{e}^-$ b) $\text{APS} + \text{P}_i \rightarrow \text{SO}_3^{2-} + \text{ADP} + \text{H}^+$ c) $\text{ADP} \rightarrow \frac{1}{2}\text{AMP} + \frac{1}{2}\text{ATP}$ $\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$		a) adenosine phosphosulfate reductase; FAD, FeS, b) sulfate adenyllyl transferase; Mg ⁺⁺ , c) adenylate kinase, Mg ⁺⁺	<i>Thiobacillus</i>
			$\Sigma = \text{HSO}_3^- + \frac{1}{2}\text{O}_2 + \text{P}_i + \frac{1}{2}\text{AMP} + \text{H}^+ \rightarrow \text{SO}_3^{2-} + \frac{1}{2}\text{ATP} + \text{H}_2\text{O}$	-227		
Ammonia	NH_3/NH_2	+900	a) $\text{NH}_3 + \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{NH}_2\text{OH} + \text{H}_2\text{O}$ b) $\text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + 5 \text{H}^+ + 4 \text{e}^-$ $\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$		a) NH ₃ monooxygenase; Cu, b) hydroxylamine: cytochrome <i>c₅₅₁</i> oxidoreductase, heme-Fe, Mo ⁺⁺	nitrosofying bacteria, e.g. <i>Nitrosomonas</i>
	NO_2/NH_2	+60				
		+340	$\Sigma = \text{NH}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + \text{H}^+$	-276		
Nitrite	$\text{NO}_2^-/\text{NO}_3^-$	+430	$\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2 \text{H}^+ + 2 \text{e}^-$		nitrite: cytochrome <i>c₅₅₀</i> oxidoreductase; heme-Fe, Mo ⁺⁺	nitrifying bacteria: e.g., <i>Nitrobacter</i>
			$\frac{1}{2}\text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$			
			$\Sigma = \text{NO}_2^- + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_3^-$	-75		
Fe^{2+} at low pH (ca.2.0)	$\text{Fe}^{3+}/\text{Fe}^{2+}$	+770	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$		rusticyanin; Cu	<i>Thiobacillus ferrooxidans</i> , <i>Sulfolobus</i>
	$\text{O}_2 (0.21 \text{ atm})/\text{H}_2\text{O}$	+1100	$\frac{1}{4}\text{O}_2 + \text{e}^- + \text{H}^+ \rightarrow \frac{1}{2}\text{H}_2\text{O}$			
			$\Sigma = \text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O}$	-32		
Fe^{2+} at ca. neutral pH	$\text{Fe(OH)}_3 \text{ (sat.)}/\text{Fe}^{2+}$	-	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{H}^+$?	?	<i>Gallionella</i>
	(10 $\mu\text{mol/l}$)	150				
Mn^{2+} at ca. neutral pH	$\text{MnO}_4^-/\text{Mn}^{2+}$?	unknown	?	?	marine <i>Pseudomonas</i>

* These reactions proceed from reduced to oxidized state

** Calculated from $\Delta E^\circ_{\text{red}}$ or from free energies of formation per mole of substrate oxidized