ENVE 424
Anaerobic Treatment

Lecture 4
Stoichiometry

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Energy Reactions

- Microorganisms obtain their energy from oxidation – reduction reactions
- Oxidation-reduction reactions always involve an electron donor and an electron acceptor
- Depending on the electron acceptor, the energy gained from 1 mole of electron donor may vary greatly

Energy Reactions

	Free Energy (kJ/mol glucose)
Aerobic Oxidation $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	-2880
Denitrification $5C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 30CO_2 + 42H_2O + 12N_2$	-2720
Sulfate Reduction $2C_6H_{12}O_6 + 6SO_4^{2-} + 9H^+ \rightarrow 12CO_2 + 12H_2O + 3H_2S + 3HS^-$	-492
Methanogenesis $C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$	-428
Ethanol Fermentation $C_6H_{12}O_6 \rightarrow 2CO_2 + 2CH_3CH_2OH$	-244

Energy Reactions

- Microorganisms would like to obtain as much energy from a reaction as possible; therefore, they would prefer to use oxygen as an electron acceptor
- However, some microorganisms cannot use oxygen as an electron acceptor.

Energy Reactions

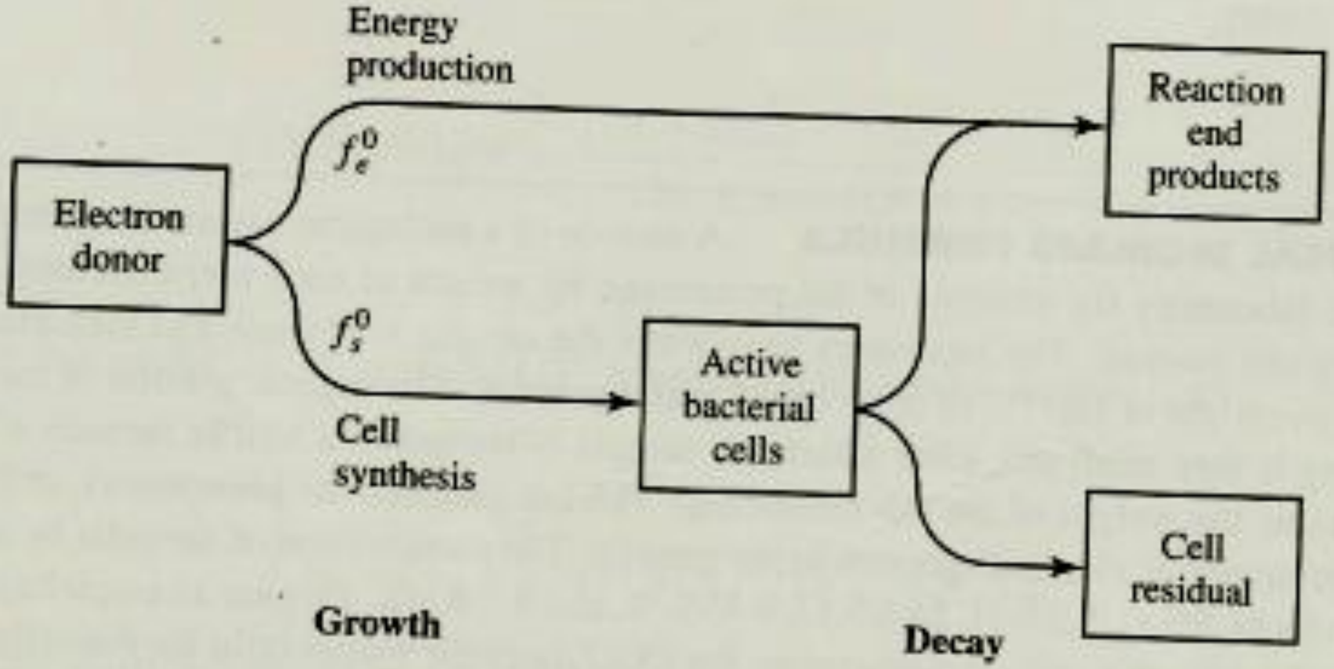


Figure 2.1 Utilization of electron donor for energy production and synthesis.

Ref:Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill. 2001.

Energy Reactions

$$Re=Ra-Rd$$

$$Rs=Rc-Rd$$

- Rd: Electron donor half reaction
- Ra: Electron acceptor half reaction
- Rc: Cell half reaction
- Re: Energy reaction
- Rs: Synthesis reaction

Energy Reactions

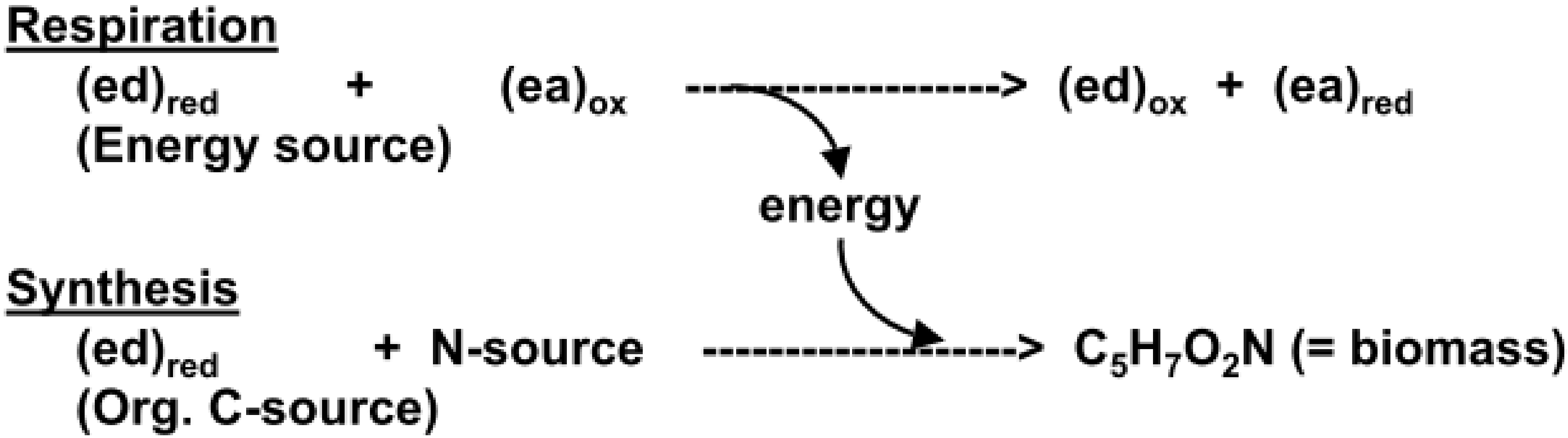
Overall reaction: $R = f_e (R_a - R_d) + f_s (R_c - R_d)$

where: f_e : fraction of electron donor used for energy production
f_s : fraction of electron donor used for cell synthesis

By definition: $f_s + f_e = 1$

Then: $R = f_e R_a + f_s R_c - R_d$

Energy Reactions



Respiration

$(ed)_{red}$ + $(ea)_{ox}$ --------------------> $(ed)_{ox}$ + $(ea)_{red}$

(Energy source)

energy

Synthesis

$(ed)_{red}$ + N-source --------------------> $C_5H_7O_2N$ (= biomass)

(Org. C-source)

Fermentation Reactions

- In fermentation, an organic compound serves as electron donor and electron acceptor
- Ethanol fermentation from glucose
- 1 mole of glucose → 2 mols ethanol + 2 mols CO_2
- All the electrons starting in glucose must end up in ethanol
- Donor: Glucose – Half Reaction
- Acceptor: Ethanol – Half Reaction

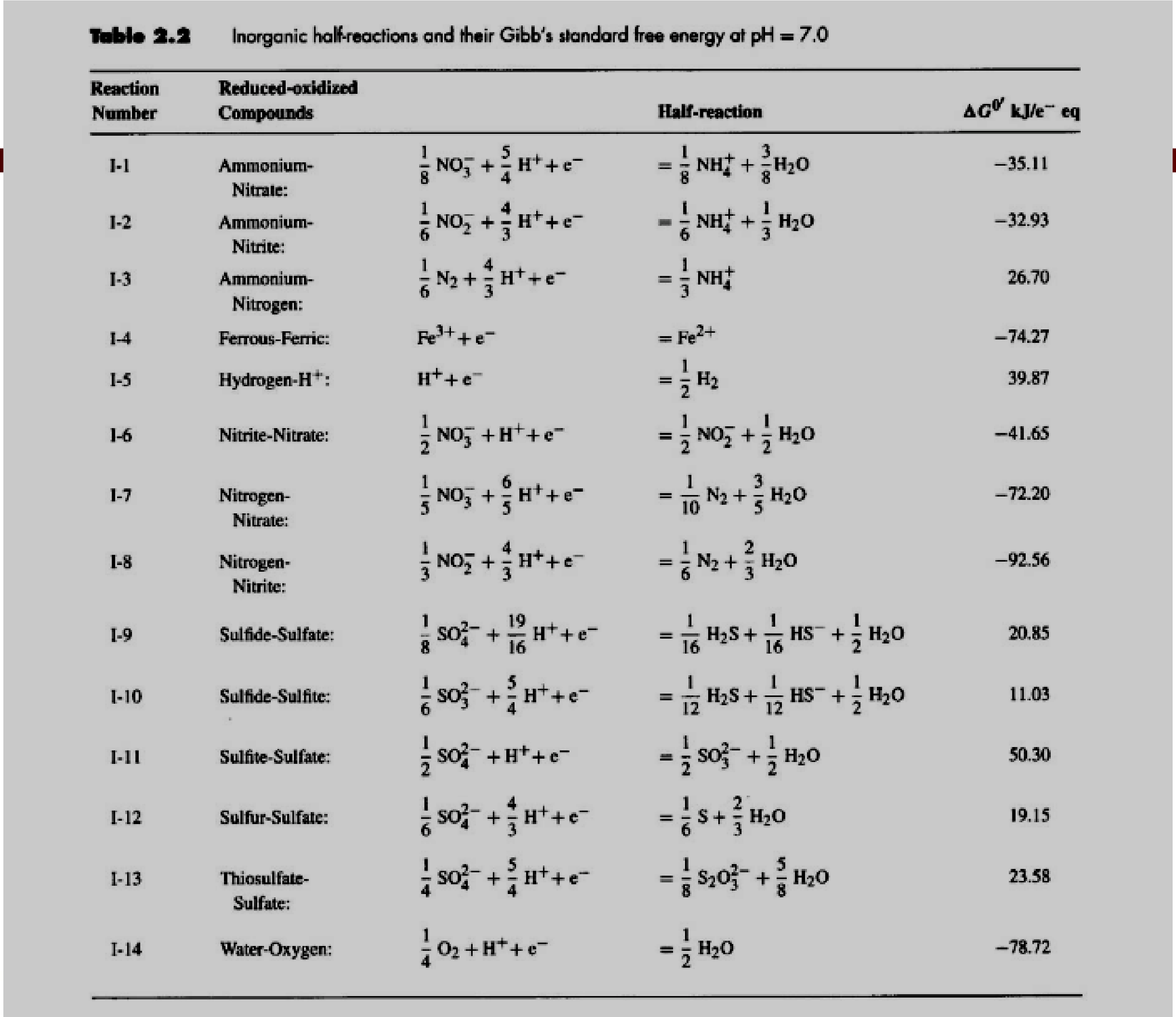


Table 2.2 Inorganic half-reactions and their Gibb's standard free energy at pH = 7.0

Reaction Number	Reduced-oxidized Compounds		Half-reaction	$\Delta G^{0'}$ kJ/e$^-$ eq
I-1	Ammonium-Nitrate:	$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	$= \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	−35.11
I-2	Ammonium-Nitrite:	$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	−32.93
I-3	Ammonium-Nitrogen:	$\frac{1}{6}N_2 + \frac{4}{3}H^+ + e^-$	$= \frac{1}{3}NH_4^+$	26.70
I-4	Ferrous-Ferric:	$Fe^{3+} + e^-$	$= Fe^{2+}$	−74.27
I-5	Hydrogen-H$^+$:	$H^+ + e^-$	$= \frac{1}{2}H_2$	39.87
I-6	Nitrite-Nitrate:	$\frac{1}{2}NO_3^- + H^+ + e^-$	$= \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	−41.65
I-7	Nitrogen-Nitrate:	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	$= \frac{1}{10}N_2 + \frac{3}{5}H_2O$	−72.20
I-8	Nitrogen-Nitrite:	$\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}N_2 + \frac{2}{3}H_2O$	−92.56
I-9	Sulfide-Sulfate:	$\frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^-$	$= \frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	20.85
I-10	Sulfide-Sulfite:	$\frac{1}{6}SO_3^{2-} + \frac{5}{4}H^+ + e^-$	$= \frac{1}{12}H_2S + \frac{1}{12}HS^- + \frac{1}{2}H_2O$	11.03
I-11	Sulfite-Sulfate:	$\frac{1}{2}SO_4^{2-} + H^+ + e^-$	$= \frac{1}{2}SO_3^{2-} + \frac{1}{2}H_2O$	50.30
I-12	Sulfur-Sulfate:	$\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}S + \frac{2}{3}H_2O$	19.15
I-13	Thiosulfate-Sulfate:	$\frac{1}{4}SO_4^{2-} + \frac{5}{4}H^+ + e^-$	$= \frac{1}{8}S_2O_3^{2-} + \frac{5}{8}H_2O$	23.58
I-14	Water-Oxygen:	$\frac{1}{4}O_2 + H^+ + e^-$	$= \frac{1}{2}H_2O$	−78.72

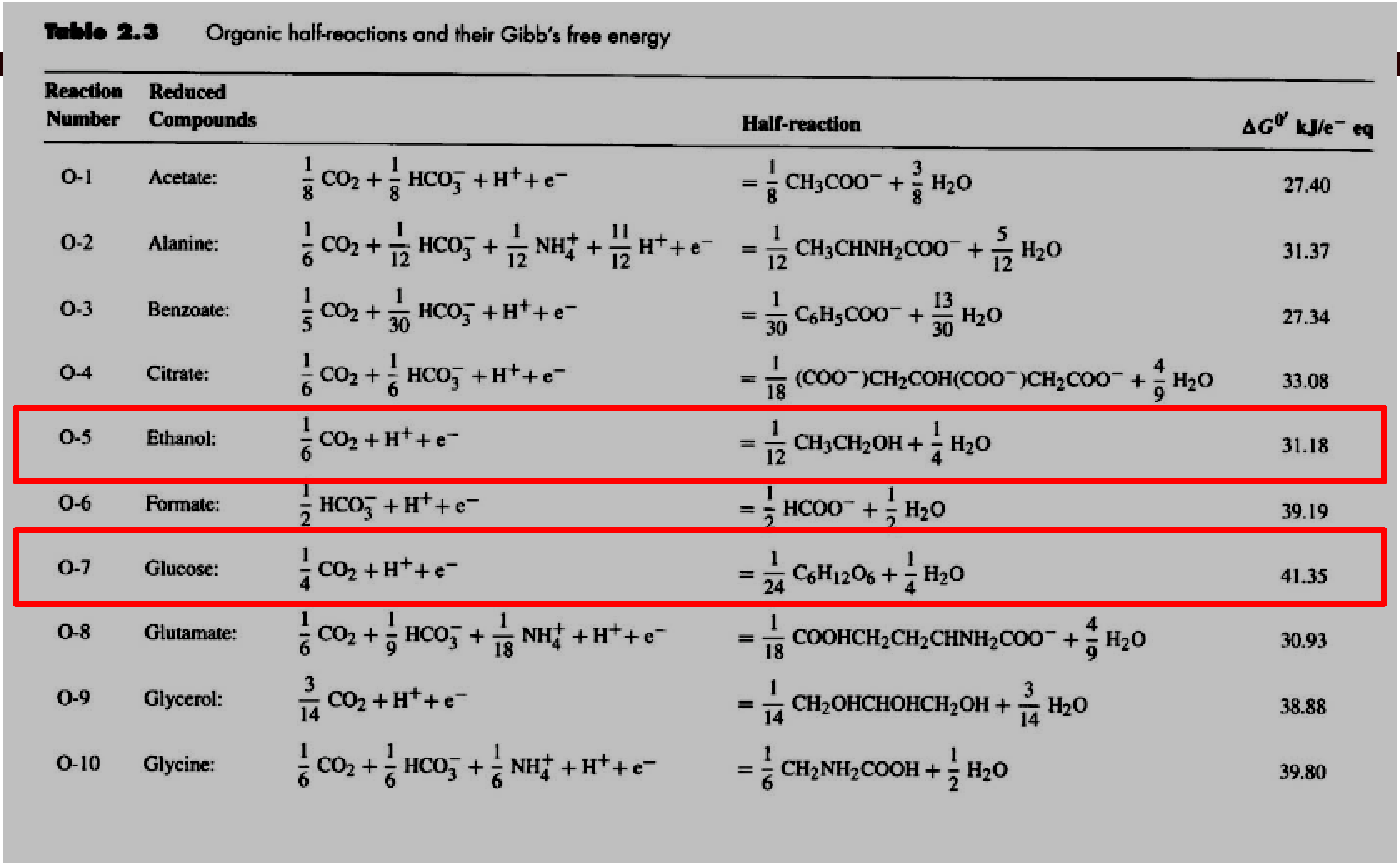


Table 2.3 Organic half-reactions and their Gibb's free energy

Reaction Number	Reduced Compounds		Half-reaction	$\Delta G^{0'}$ kJ/e⁻ eq
O-1	Acetate:	$\frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$	$= \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O$	27.40
O-2	Alanine:	$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + \frac{1}{12}NH_4^+ + \frac{11}{12}H^+ + e^-$	$= \frac{1}{12}CH_3CHNH_2COO^- + \frac{5}{12}H_2O$	31.37
O-3	Benzoate:	$\frac{1}{5}CO_2 + \frac{1}{30}HCO_3^- + H^+ + e^-$	$= \frac{1}{30}C_6H_5COO^- + \frac{13}{30}H_2O$	27.34
O-4	Citrate:	$\frac{1}{6}CO_2 + \frac{1}{6}HCO_3^- + H^+ + e^-$	$= \frac{1}{18}(COO^-)CH_2COH(COO^-)CH_2COO^- + \frac{4}{9}H_2O$	33.08
O-5	Ethanol:	$\frac{1}{6}CO_2 + H^+ + e^-$	$= \frac{1}{12}CH_3CH_2OH + \frac{1}{4}H_2O$	31.18
O-6	Formate:	$\frac{1}{2}HCO_3^- + H^+ + e^-$	$= \frac{1}{2}HCOO^- + \frac{1}{2}H_2O$	39.19
O-7	Glucose:	$\frac{1}{4}CO_2 + H^+ + e^-$	$= \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O$	41.35
O-8	Glutamate:	$\frac{1}{6}CO_2 + \frac{1}{9}HCO_3^- + \frac{1}{18}NH_4^+ + H^+ + e^-$	$= \frac{1}{18}COOHCH_2CH_2CHNH_2COO^- + \frac{4}{9}H_2O$	30.93
O-9	Glycerol:	$\frac{3}{14}CO_2 + H^+ + e^-$	$= \frac{1}{14}CH_2OHCHOHCH_2OH + \frac{3}{14}H_2O$	38.88
O-10	Glycine:	$\frac{1}{6}CO_2 + \frac{1}{6}HCO_3^- + \frac{1}{6}NH_4^+ + H^+ + e^-$	$= \frac{1}{6}CH_2NH_2COOH + \frac{1}{2}H_2O$	39.80

Table 2.3 (Continued)

O-11	Lactate:	$\frac{1}{6}CO_2 + \frac{1}{12} HCO_3^- + H^+ + e^-$	$= \frac{1}{12} CH_3CHOHCOO^- + \frac{1}{3} H_2O$	32.29
O-12	Methane:	$\frac{1}{8} CO_2 + H^+ + e^-$	$= \frac{1}{8} CH_4 + \frac{1}{4} H_2O$	23.53
O-13	Methanol:	$\frac{1}{6} CO_2 + H^+ + e^-$	$= \frac{1}{6} CH_3OH + \frac{1}{6} H_2O$	36.84
O-14	Palmitate:	$\frac{15}{\cancel{19}} CO_2 + \frac{1}{92} HCO_3^- + H^+ + e^-$ 92	$= \frac{1}{92} CH_3(CH_2)_{14}COO^- + \frac{31}{92} H_2O$	27.26
O-15	Propionate:	$\frac{1}{7} CO_2 + \frac{1}{14} HCO_3^- + H^+ + e^-$	$= \frac{1}{14} CH_3CH_2COO^- + \frac{5}{14} H_2O$	27.63
O-16	Pyruvate:	$\frac{1}{5} CO_2 + \frac{1}{10} HCO_3^- + H^+ + e^-$	$= \frac{1}{10} CH_3COCOO^- + \frac{2}{5} H_2O$	35.09
O-17	Succinate:	$\frac{1}{7} CO_2 + \frac{1}{7} HCO_3^- + H^+ + e^-$	$= \frac{1}{14} (CH_2)_2(COO^-)_2 + \frac{3}{7} H_2O$	29.09
O-18	Domestic Wastewater:	$\frac{9}{50} CO_2 + \frac{1}{50} NH_4^+ + \frac{1}{50} HCO_3^- + H^+ + e^-$	$= \frac{1}{50} C_{10}H_{19}O_3N + \frac{9}{25} H_2O$	*
O-19	Custom Organic Half Reaction:	$\frac{(n-c)}{d} CO_2 + \frac{c}{d} NH_4^+ + \frac{c}{d} HCO_3^- + H^+ + e^-$	$= \frac{1}{d} C_nH_aO_bN_c + \frac{2n-b+c}{d} H_2O$ where, $d = (4n + a - 2b - 3c)$	*
O-20	Cell Synthesis:	$\frac{1}{5} CO_2 + \frac{1}{20} NH_4^+ + \frac{1}{20} HCO_3^- + H^+ + e^-$	$= \frac{1}{20} C_5H_7O_2N + \frac{9}{20} H_2O$	*

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*Equations O-18 to O-20 do not have $\Delta G^{0'}$ values because the reduced species is not chemically defined.

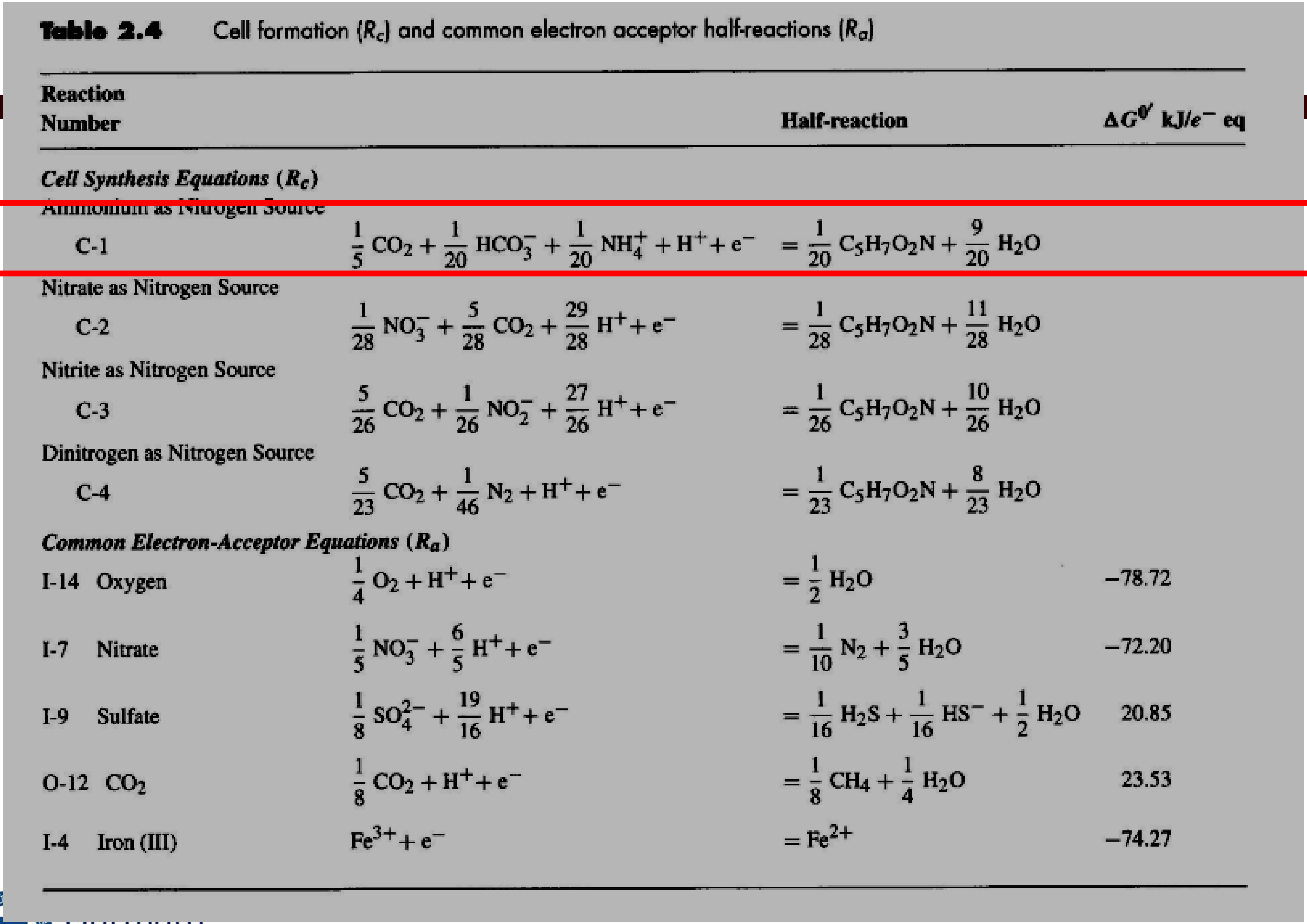

Table 2.4 Cell formation (R_c) and common electron acceptor half-reactions (R_a)

Reaction Number	Half-reaction	$\Delta G^{0\prime}$ kJ/e^- eq
Cell Synthesis Equations (R_c)		
Ammonium as Nitrogen Source		
C-1	$\frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^- = \frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$	
Nitrate as Nitrogen Source		
C-2	$\frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^- = \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$	
Nitrite as Nitrogen Source		
C-3	$\frac{5}{26}CO_2 + \frac{1}{26}NO_2^- + \frac{27}{26}H^+ + e^- = \frac{1}{26}C_5H_7O_2N + \frac{10}{26}H_2O$	
Dinitrogen as Nitrogen Source		
C-4	$\frac{5}{23}CO_2 + \frac{1}{46}N_2 + H^+ + e^- = \frac{1}{23}C_5H_7O_2N + \frac{8}{23}H_2O$	
Common Electron-Acceptor Equations (R_a)		
I-14 Oxygen	$\frac{1}{4}O_2 + H^+ + e^- = \frac{1}{2}H_2O$	−78.72
I-7 Nitrate	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O$	−72.20
I-9 Sulfate	$\frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^- = \frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	20.85
O-12 CO_2	$\frac{1}{8}CO_2 + H^+ + e^- = \frac{1}{8}CH_4 + \frac{1}{4}H_2O$	23.53
I-4 Iron (III)	$Fe^{3+} + e^- = Fe^{2+}$	−74.27

Fermentation Reactions

- Ethanol fermentation from glucose (biomass synthesis is not included)

$$Ra: \frac{1}{6}CO_2 + H^+ + e^- \rightarrow \frac{1}{12}CH_3CH_2OH + \frac{1}{4}H_2O$$

$$-Rd: \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^-$$

$$Re: \frac{1}{24}C_6H_{12}O_6 \rightarrow \frac{1}{12}CH_3CH_2OH + \frac{1}{12}CO_2$$

Fermentation Reactions

- Ethanol fermentation from glucose (biomass synthesis is **included**)
- Assume fs=0.22, fe=0.78

$$feRa: 0.78\frac{1}{6}CO_2 + 0.78H^+ + 0.78e^- \rightarrow 0.78\frac{1}{12}CH_3CH_2OH + 0.78\frac{1}{4}H_2O$$

$$-Rd: \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^-$$

$$fsRc: 0.22\frac{1}{5}CO_2 + 0.22\frac{1}{20}HCO_3^- + 0.22\frac{1}{20}NH_4^+ + 0.22H^+ + 0.22e^-$$

$$\rightarrow\ 0.22\frac{1}{20}C_5H_7O_2N + 0.22\frac{9}{20}H_2O$$

Fermentation Reactions

- Ethanol fermentation from glucose (biomass synthesis is **included**)
- Assume fs=0.22, fe=0.78

$$feRa: 0.78\frac{1}{6}CO_2 + 0.78H^+ + 0.78e^- \rightarrow 0.78\frac{1}{12}CH_3CH_2OH + 0.78\frac{1}{4}H_2O$$

$$-Rd: \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^-$$

$$0.22Rc: 0.044CO_2 + 0.011HCO_3^- + 0.011NH_4^+ + 0.22H^+ + 0.22e^-$$

$$\rightarrow\ 0.011C_5H_7O_2N + 0.099H_2O$$

$$R: 0.0417C_6H_{12}O_6 + 0.011NH_4^+ + 0.011HCO_3^-$$

$$\rightarrow\ 0.011C_5H_7O_2N + 0.065CH_3CH_2OH + 0.076CO_2 + 0.044H_2O$$

Methanogenic Reactions

- Acetate to Methane

$$CH_3 \vdots COO^- + \ H_2O \rightarrow CH_4 + HCO_3^-$$

$$-Rd\colon \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O \rightarrow \frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$$

$$Ra\colon \frac{1}{8}CO_2 + H^+ + e^- \rightarrow \frac{1}{8}CH_4 + \frac{1}{4}H_2O$$

$$R\colon \frac{1}{8}CH_3COO^- + \frac{1}{8}H_2O \rightarrow \frac{1}{8}CH_4 + \frac{1}{8}HCO_3^-$$

Methanogenic Reactions

- Each g of BOD_L generates 0.35 L CH_4 at STP (0°C, 1 atm)
- The energy value of methane is 35.8 kJ/L at STP

- Typical loading to anaerobic digestors, 5 – 10 kg COD/d.m^3
- Typical loading for an aerobic treatment < 1 kg COD/d.m^3

Properties of Methane

Colorless
Odorless
Non-poisonous (simple asphyxiant)
Flammable

Explosive mixture: 1 vol. CH_4 /10 vol. Air (or 2 vol. O_2)

Air with < 5.5% CH_4 : no explosion

Air with > 14% CH_4 : burns without noise

Heat of combustion = 978 BTU/ft^3 @ 25^{o}C (1 kg CH_4 = 13,300 kcal)

Example 1

- Industrial wastewater with a flow of 10^4 m^3/d and a BODL of 20,000 mg/L is being treated. Assuming the waste stabilization is 90%, please calculate the methane content. Please calculate the energy value of the produced methane

Example 2

- A wastewater from food processing contains 1.0 M glucose. For operation of an anaerobic treatment processes for this wastewater, estimate the methane production, the mass of biological cells produced, and the concentration of ammonia-N required for cell growth for m^3 of wastewater treated. Assume that fs=0.2 and glucose is completely consumed.