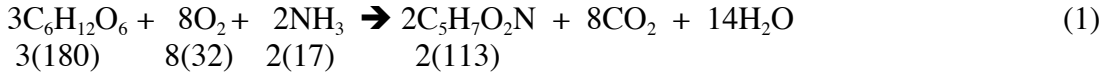


THERMODYNAMICS & STOICHIOMETRY

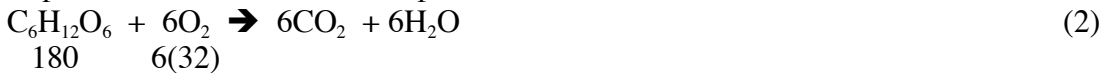
Estimating Yield & Electron Acceptor Requirements from Stoichiometry



$$Y_{(\text{glucose})} = \frac{\square \text{ cells}}{\square \text{ glucose}} = \frac{2(113 \text{ g/mole})}{3(180 \text{ g/mole})} = 0.42 \text{ g cells/g glucose used}$$

Calculate Electron Acceptor Equivalent of Electron Donor

Express Yield on Electron Acceptor basis:



$$e^- \text{ Acceptor Equivalent of glucose is: } \frac{\square (\text{O}_2)}{\square \text{ glucose}} = \frac{6(32 \text{ g/mole})}{180 \text{ g/mole}} = 1.07 \text{ g O}_2/\text{g glucose} \quad (3)$$

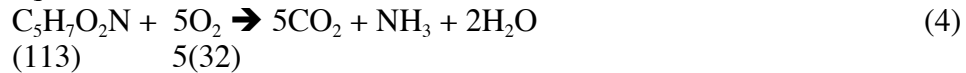
$\frac{6(32 \text{ g/mole})}{180 \text{ g/mole}}$

$$Y_{(\text{TEA})} = \frac{\square \text{ cells}}{\square \text{ glucose as } e^- \text{ AE}} = \frac{2(113 \text{ g/mole})}{3(180 \text{ g/mole}) (1.07 \text{ g O}_2/\text{g glucose})} = \frac{0.39 \text{ g cells}}{\text{g } (e^- \text{ AE}) \text{ used}}$$

Note: Actual yield < $Y_{(e^- \text{ AE})}$ as portion of substrate is oxidized for energy w/time

Consider Electron Acceptor (Oxygen):

1. used for substrate oxidation to CO_2 and H_2O
2. equivalent of biomass



$$(e^- \text{ AE}) \text{ of biomass} = \frac{\square (\text{O}_2)}{\square (\text{C}_5\text{H}_7\text{O}_2\text{N})} = \frac{5(32 \text{ g/mole})}{113 \text{ g/mole}} = 1.42 \text{ g O}_2/\text{g cells}$$

3. substrate (e^- donor as $e^- \text{ AE}$) **not** transformed to CO_2 and H_2O

Refer to Eqn (1): Glucose is NOT totally oxidized to CO_2 & H_2O as some C, H, and O are incorporated into cells. Oxygen actually utilized in Eqn (1) is: total glucose oxygen demand ($e^- \text{ AE}$ of e^- donor) – cells formed ($e^- \text{ AE}$ of biomass):

$$(e^- \text{ AE}) \text{ utilized} = (e^- \text{ AE}) \text{ cells} + (e^- \text{ AE}) \text{ of oxidized substrate} \quad (5)$$

$$(e^- \text{ AE}) \text{ of oxidized substrate} = (e^- \text{ AE}) \text{ utilized} - (e^- \text{ AE}) \text{ cells} \quad (6)$$

$$= \frac{1.07 \text{ g O}_2}{\text{g glucose}} \times \frac{3 \text{ moles } (180 \text{ g glucose})}{\text{mole glucose}} - \frac{1.42 \text{ g O}_2}{\text{g cells}} \times \frac{2 \text{ moles } (113 \text{ g cells})}{\text{mole cells}}$$

$$= 577.8 \text{ g O}_2 - 320.9 \text{ g O}_2 = 256.9 \text{ g O}_2$$

Electron Acceptor Equivalent of Electron Donor is shown as $(e^-AE)_{donor}$

Now, O_2 actually used per unit of (e^-AE) (Eqn 1) used is:

$$\frac{\text{Oxygen consumed}}{(e^-AE) \text{ glucose}} = \frac{256.9 \text{ g } O_2}{3 \text{ mole } (1.07 \text{ g } (e^-AE) / \text{g glucose}) (180 \text{ g/mole})} = 0.44 \text{ g } O_2 / \text{g } (e^-AE) \text{ used}$$

0.44 is less than 1 because of substrate incorporated into cells and not oxidized!

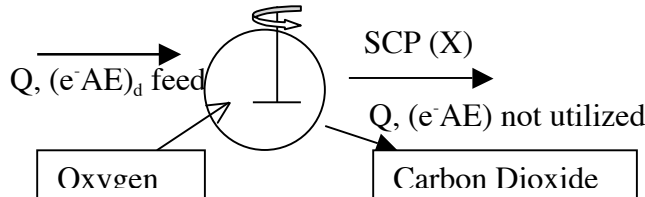
EXAMPLE 1. Observed Cell YIELD & Electron Acceptor (OXYGEN) used

Reactor: Chemostat (p. 190) Aerobic, CFSTR, without recycle

Conditions: Feedstock (e^-AE) 500 g/m^3 ; $F = 1000 \text{ m}^3/\text{d}$; (e^-AE) not utilized = 10 g/m^3 ;

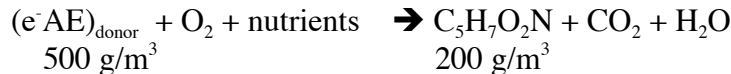
Effluent single cell protein (SCP, as X) = 200 g/m^3

- Find:
- Y (obs) as $\text{g SCP/g } (e^-AE)$ utilized
 - Oxygen used as $(\text{g } O_2 / \text{g } e^-AE \text{ removed})$ and as $(\text{g } O_2 / \text{day})$



Solution:

- Y (observed):



$$\text{Mass of X} = (\text{SCP}, X) (F)$$

- $\text{g SCP produced/d} = 200 \text{ g/m}^3 (1000 \text{ m}^3/\text{d}) = 200,000 \text{ g SCP/d}$
- $\text{g } (e^-AE)_d \text{ removed/d} = (500 - 10) \text{ g } (e^-AE) / \text{m}^3 (1000 \text{ m}^3/\text{d}) = 490,000 \text{ g } (e^-AE) / \text{d}$
- $Y_{obs} = \frac{200,000 \text{ g SCP/d}}{490,000 \text{ g/d } (e^-AE)} = 0.41 \text{ g SCP/g } (e^-AE)_d \text{ removed}$

- Oxygen used as $\text{g } O_2$ per d:

- $(e^-AE)_d$ mass balance (steady state) around complex-mix (no recycle) reactor:
accumulation = in - out - conversion to SCP

$$0 = (e^-AE) \text{ in} - (e^-AE) \text{ out} - \text{oxygen equivalent of SCP}$$

$$0 = (500 - 10) \text{ g/m}^3 (1000 \text{ m}^3/\text{d}) - 200,000 \text{ g SCP/d} (1.42 \text{ g } O_2/\text{g SCP})$$

$$0 = 490,000 \text{ g/d} - 284,000 \text{ g/d} = 206,000 \text{ g } O_2/\text{d}$$

- Oxygen used in $\text{g } O_2$ per $(e^-AE)_d$ removed:

$$\text{Oxygen/COD} = \frac{206,000 \text{ g/d used}}{490,000 \text{ g } e^-AE/\text{day removed}} = 0.42 \text{ g } O_2/\text{g } (e^-AE)_d$$

NOTE: $(e^-AE)_d$ Balance that accounts for cell production & oxidation is:

$$\text{g } (e^-AE) \text{ Cells} + \text{g } (e^-AE)_d \text{ oxidized} = \text{g } (e^-AE) \text{ removed}$$

$$(0.41 \text{ g SCP/g } e^-AE_d) (1.42 \text{ g } O_2/\text{g SCP}) + 0.42 \text{ g } O_2/\text{g } e^-AE_d = 1.0 \text{ g } O_2/\text{g } e^-AE_d$$

End of Example 1

Stoichiometry of Biological Reactions

$$\mathbf{R} = \mathbf{fe Ra} + \mathbf{fs Rcs} - \mathbf{Rd} \quad (7)$$

R = overall balanced reaction

fe = fraction of electron donor used for energy

Ra = half-reaction for electron acceptor

fs = fraction of electron donor used for cell synthesis

Rcs = half reaction for cell synthesis

Rd = half reaction for electron donor

$$\mathbf{fe} + \mathbf{fs} = 1 \quad (8)$$

EXAMPLE 2 Write a Balanced Reaction for the Aerobic Biological Conversion of Acetate To Cells Using NH₃ as the Nutrient Source

Given: Eqn 7 and half-reactions in Table; aerobic conditions; NH₃
fe = 0.41; fs = 0.59

1. Balanced Stoichiometric Equation:

$$\mathbf{R} = \mathbf{feRa} + \mathbf{fs Rcs} - \mathbf{Rd}$$

$$\mathbf{feRa} = (0.41) (1/4\text{O}_2 + \text{H} + \text{e} \rightarrow 1/2 \text{H}_2\text{O}) = 0.103\text{O}_2 + 0.41\text{H} + 0.41\text{e} \rightarrow 0.205\text{H}_2\text{O}$$

$$\begin{aligned} \mathbf{fsRcs} &= (0.59) (1/5\text{CO}_2 + 1/20\text{HCO}_3 + 1/20\text{NH}_4 + \text{H} + \text{e} \rightarrow 1/20\text{C}_5\text{H}_7\text{O}_2\text{N} + 9/20\text{H}_2\text{O}) \\ &= 0.118\text{CO}_2 + 0.0295\text{HCO}_3 + 0.0295\text{NH}_4 + 0.59\text{H} + 0.59\text{e} \rightarrow \\ &\quad 0.0295\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.2655\text{H}_2\text{O} \end{aligned}$$

$$-\mathbf{Rd} = 0.125\text{CH}_3\text{COO} + 0.375\text{H}_2\text{O} \rightarrow 0.125\text{CO}_2 + 0.125\text{HCO}_3 + \text{H} + \text{e}$$

$$\mathbf{R} = 0.125 \text{CH}_3\text{COO} + 0.0295 \text{NH}_4 + 0.103 \text{O}_2 \rightarrow 0.0295 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.0955 \text{H}_2\text{O} + 0.095 \text{HCO}_3 + 0.007 \text{CO}_2$$

2. Calculate Cell Yield based on acetate (Ac) and (e⁻AE)_{Ac}:

$$\mathbf{Yield:} \quad \frac{0.0295 \text{ mol cell (113 g/mol cell)}}{0.125 \text{ mol Ac (60 g/mol Ac)}} = \frac{3.33 \text{ g cells}}{7.5 \text{ g Ac}} = \mathbf{0.44 \text{ g cells/g Ac}}$$

$$\begin{aligned} \mathbf{Y(e^-AE)_{Ac}:} & \quad (\text{e}^- \text{AE})_{Ac}: 0.125 \text{ mol Ac (60g/mol)}(1.07 \text{ g O}_2/\text{g AC}) = \mathbf{8.03 \text{ g as (e}^- \text{AE)}} \\ \text{Cal. (e}^- \text{AE)}_{Ac}: & \quad \underline{\text{CH}_3\text{COOH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}} \quad [\text{O/Ac} = 64/60 = 1.07 \text{ gO}_2/\text{gAc}] \end{aligned}$$

$$\mathbf{Y(e^-AE)_{Ac}} = \frac{3.334 \text{ g Cells}}{8.03 \text{ g as (e}^- \text{AE)}} = \mathbf{0.42 \text{ g Cells/g (e}^- \text{AE)}_{Ac}}$$

$$\mathbf{Nutrient Requirement:} \quad \frac{0.0295 \text{ mol (14 g/mol N)}}{0.0295 \text{ mol (113 g/mol cell)}} = \frac{0.413 \text{ g N}}{3.33 \text{ g cells}} = \mathbf{0.12 \text{ g N/g cells}}$$

Oxygen Requirement: $\frac{0.103 \text{ mol (32 g/mol O}_2\text{)}}{0.0295 \text{ mol (113 g/mol cell)}} = \frac{3.296 \text{ g O}_2}{3.33 \text{ g cells}} = \frac{1 \text{ g O}_2}{\text{g cells}}$

Estimating Biomass Yield from Bioenergetics

Key steps in bioenergetics analysis:

1. Identify electron donor
2. Calc. energy (E) produced from bacterial redox reaction
3. Calc. E needed for converting growth carbon source to cell matter
4. Calc. Cell Yield based on balance between E prod and E needed for synthesis

Amount of E needed for cell synthesis = f (carbon source, nitrogen source)

Pyruvate is used as the intermediate for cell synthesis in this analysis

Energy for Cell Synthesis: $\Delta G_s = \frac{\Delta G_p}{K^m} + \frac{\Delta G_N}{K}$ $\Delta G = \text{Free Energy}$ (9)

Where $\Delta G_s =$ convert 1 (eeq) of carbon source to cell matter

$\Delta G_p =$ convert 1 (eeq) of carbon source to pyruvate
 = calc. using ΔG half reactions to convert carbon source to pyruvate

$K =$ fraction of energy captured (remainder as heat/entropy), assume 0.6

$m = +1$ if $\Delta G_p > 0$ (endergonic) ; -1 if $\Delta G_p < 0$ (exergonic)

$\Delta G_c =$ to convert 1 (eeq) of pyruvate to 1 (eeq) of cell
 (+31.41 kJ/eeq cell)

$\Delta G_N =$ per eeq of cells to reduce nitrogen used to ammonia (kJ/eeq)
 = +17.46 for NO_3 , +13.61 for NO_2 , +15.85 for N_2 , 0 for NH_4

Electron Donor – fraction used for energy (fe); fraction used for cell synthesis (fs)

Equation relating energy made available (left side) = energy for synthesis (right side)

$K \Delta G_R (fe/fs) = - \Delta G_S$ where $fe + fs = 1$ (10), (8)

$K =$ fraction of energy captured (assume 0.6)

$\Delta G_R =$ energy released from redox reactions, kJ/mole e transferred

$fe =$ e mole fraction of substrate used for energy

$fs =$ e mole fraction of substrate used for synthesis

$\Delta G_S =$ energy used for cell synthesis (growth), kJ/mole e transfer for cell growth

EXAMPLE 3 - Estimate Biomass Yield Using Bioenergetics
Calculate growth on acetate with O₂ as electron acceptor

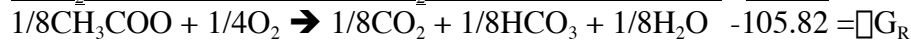
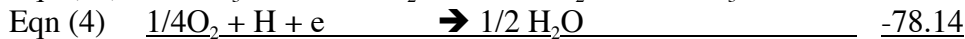
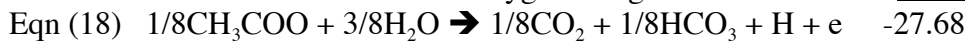
Given: Cell YIELD for acetate as carbon source (e⁻ donor); heterotrophs; **aerobic**; NH₄⁺ nutrient

1. g cells as (e⁻AE)_{Ac}/g (e⁻AE)_{Ac} utilized
2. g cells /g (e⁻AE)_{Ac} utilized

(1) Calc. K ΔG_R with O₂ as electron acceptor

$$K \Delta G_R (fe/fs) = - \Delta G_S \quad \text{where } fe + fs = 1 \quad (10), (8)$$

Solve for acetate redox reaction with oxygen using Table kJ/mole e



Calc. energy produced & captured by cell = **KΔG_R** = (0.60) (-105.82) = **-63.42 kJ/mole e**

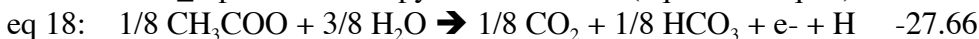
(2) Calc. energy needed per e⁻ mole of cell ΔG_S: ΔG_S = ΔG_p + ΔG_c + ΔG_N (9)

$$\frac{\Delta G_p}{K_m} + \frac{\Delta G_c}{K}$$

ΔG_N = 0 (NH₃ as nitrogen source)

ΔG_c = 31.41 kJ/mole eeq cell (pyruvate to cell)

ΔG_p = acetate to pyruvate reaction (eq 18 and eq 15) kJ/mole e



ΔG_p = + 8.12

Because ΔG_p>0 ==> m = +1 (energy is required)

Calc. ΔG_S = $[\frac{8.12}{(0.6)^{+1}} + 31.41 + 0] = \mathbf{44.94 \text{ kJ/mole e-}}$

(3) Determine fe & fs with eq. (10): fe/fs = - ΔG_S/ K ΔG_R = -44.94/-63.42 = **0.707**

Since: fe + fs = 1, => fe/(1-fe) = 0.707 =>

fe = 0.707/1.707 = 0.41 [g energy (e⁻AE)_{Ac}/g (e⁻AE)_{Ac} utilized]

thus **fs = 0.59 [g cell (e⁻AE)_{Ac}/g (e⁻AE)_{Ac} utilized]**

(4) Determine yield based on (e⁻AE)_{Ac}: g cells /g e⁻AE utilized

For cells (C₅H₇O₂N), 1 g cells = 1.42 (g e⁻AE)_{cells}

Yield = $\frac{(0.59 \text{ g cell (e}^- \text{AE)}_{Ac} / \text{g (e}^- \text{AE)}_{Ac} \text{ utilized})}{(1.42 \text{ g cell (e}^- \text{AE)} / \text{g Cells})} = \mathbf{0.42 \text{ g Cells/g (e}^- \text{AE)}_{Ac} \text{ utilized}}$

EXAMPLE 4: Estimate Biomass Yield Using Bioenergetics
Calculate growth on acetate with CO₂ as electron acceptor

Given: Cell YIELD for acetate as e⁻ donor; heterotrophs; **methanogenic**;
 NH₄⁺ nutrient

1. g cells as (e⁻AE)_{Ac}/g (e⁻AE)_{Ac} utilized
2. g cells /g (e⁻AE)_{Ac} utilized

(1) Calc. K ΔG_R with CO₂ as electron acceptor

$$K \Delta G_R (fe/fs) = - \Delta G_S \quad \text{where } fe + fs = 1 \quad (10), (8)$$

Solve for acetate redox reaction with CO₂ using Table ΔG kJ/mole e

Eqn (18)	1/8CH ₃ COO + 3/8H ₂ O → 1/8CO ₂ + 1/8HCO ₃ + H + e	-27.68
Eqn (8)	1/8CO ₂ + H + e → 1/8CH ₄ + 1/8HCO ₃	+24.11



Calc. Energy captured by cell = K ΔG_R = (0.60) (-3.57) = -2.142 kJ/mole e

(2) Calc. energy needed per e⁻ mole of cell ΔG_S: ΔG_S = ΔG_p + ΔG_c + ΔG_N (9)

$$\Delta G_p = (\text{same as for acetate/O}_2) = +8.12 \text{ kJ/mole e}$$

$$\Delta G_c = +31.41 \text{ kJ/mole e cells}$$

$$\Delta G_N = 0$$

$$\Delta G_S = \left[\frac{(8.12)}{(0.6)} + 31.41 + 0 \right] = 44.94 \text{ kJ/mole e (synthesis same as for aerobic)}$$

(3) Determine fe and fs with eq. (10): fe/fs = -ΔG_S/ K ΔG_R = -44.94/-2.142 = 21.0

Since fe + fs = 1, ==> fe/ (1-fe) = 21.0 ==>

$$fe = 21 (1-fe) = \mathbf{0.954 \text{ [g energy (e}^- \text{AE)}_{Ac} / g (e}^- \text{AE)}_{Ac} \text{ utilized]}}$$

$$\text{thus } fs = 1 - \mathbf{0.954} = \mathbf{0.046 \text{ [g cell (e}^- \text{AE)}_{Ac} / g (e}^- \text{AE)}_{Ac} \text{ utilized]}}$$

(4) Determine yield based on (e⁻AE)_{Ac}: g cells /g e⁻AE utilized

For cells (C₅H₇O₂N), 1 g cells = 1.42 (g e⁻AE)_{cells}

$$\text{Yield} = \frac{(0.046 \text{ g cell (e}^- \text{AE)}_{Ac} / g (e}^- \text{AE)}_{Ac} \text{ utilized})}{(1.42 \text{ g cell (e}^- \text{AE)}_{Ac} / g \text{ Cells})} = \mathbf{0.032 \text{ g Cells/g (e}^- \text{AE)}_{Ac} \text{ utilized}}$$

(5) Compare Yields for acetate oxidation as a function of electron acceptor:

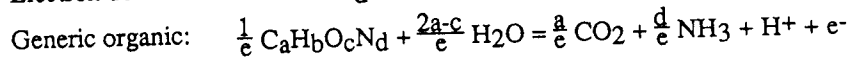
Electron acceptor	Yield, g Cell/g (e ⁻ AE) _{Ac}	Product
O ₂	0.42	CO ₂ , H ₂ O
CO ₂	0.032	CH ₄

Examples of half-reactions for construction of a balanced equation for an overall bacterial reaction.

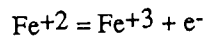
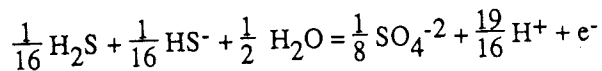
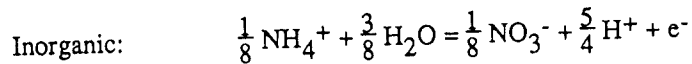
Overall Reaction:

$$R = R_d + f_e R_a + f_s R_c$$

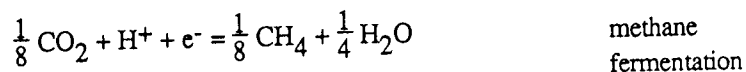
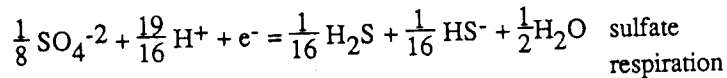
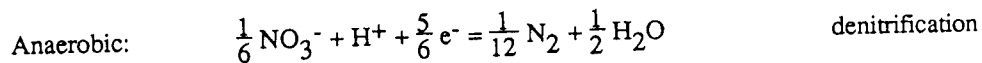
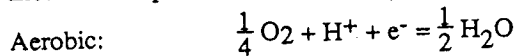
Electron donor half reactions (R_d):



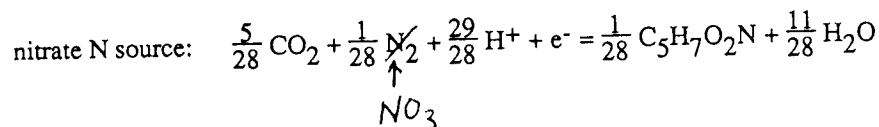
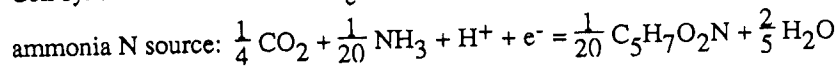
where $e = 4a + b - 2c - 3d$



Electron acceptor half reactions (R_a):



Cell synthesis half reactions (R_c):



Half reactions for biological systems^a

Reaction number	Half reaction	$\Delta G^\circ (W),^b$ kJ per electron equivalent
Reactions for bacterial cell synthesis (R_{cs})		
Ammonia as nitrogen source:		
1.	$\frac{1}{5} \text{CO}_2 + \frac{1}{20} \text{HCO}_3^- + \frac{1}{20} \text{NH}_4^+ + \text{H}^+ + \text{e}^- = \frac{1}{20} \text{C}_5\text{H}_7\text{O}_2\text{N} + \frac{9}{20} \text{H}_2\text{O}$	
Nitrate as nitrogen source:		
2.	$\frac{1}{28} \text{NO}_3^- + \frac{5}{28} \text{CO}_2 + \frac{29}{28} \text{H}^+ + \text{e}^- = \frac{1}{28} \text{C}_5\text{H}_7\text{O}_2\text{N} + \frac{11}{28} \text{H}_2\text{O}$	
Reactions for electron acceptors (R_a)		
Nitrite:		
3.	$\frac{1}{3} \text{NO}_2^- + \frac{4}{3} \text{H}^+ + \text{e}^- = \frac{1}{8} \text{N}_2 + \frac{2}{3} \text{H}_2\text{O}$	-93.23
Oxygen:		
4.	$\frac{1}{4} \text{O}_2 + \text{H}^+ + \text{e}^- = \frac{1}{2} \text{H}_2\text{O}$	-78.14
Nitrate:		
5.	$\frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + \text{e}^- = \frac{1}{10} \text{N}_2 + \frac{3}{5} \text{H}_2\text{O}$	-71.67
Sulfite:		
6.	$\frac{1}{6} \text{SO}_3^{2-} + \frac{5}{4} \text{H}^+ + \text{e}^- = \frac{1}{12} \text{H}_2\text{S} + \frac{1}{12} \text{HS}^- + \frac{1}{2} \text{H}_2\text{O}$	13.60
Sulfate:		
7.	$\frac{1}{8} \text{SO}_4^{2-} + \frac{19}{16} \text{H}^+ + \text{e}^- = \frac{1}{16} \text{H}_2\text{S} + \frac{1}{16} \text{HS}^- + \frac{1}{2} \text{H}_2\text{O}$	21.27
Carbon dioxide (methane fermentation):		
8.	$\frac{1}{8} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{8} \text{CH}_4 + \frac{1}{4} \text{H}_2\text{O}$	24.11
Reactions for electron donors (R_d)		
<i>Organic donors (heterotrophic reactions)</i>		
Domestic wastewater:		
9.	$\frac{9}{50} \text{CO}_2 + \frac{1}{50} \text{NH}_4^+ + \frac{1}{50} \text{HCO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{50} \text{C}_{10}\text{H}_{19}\text{O}_3\text{N} + \frac{9}{25} \text{H}_2\text{O}$	31.80
Protein (amino acids, proteins, nitrogenous organics):		
10.	$\frac{8}{33} \text{CO}_2 + \frac{2}{33} \text{NH}_4^+ + \frac{31}{33} \text{H}^+ + \text{e}^- = \frac{1}{66} \text{C}_{16}\text{H}_{24}\text{O}_5\text{N}_4 + \frac{27}{66} \text{H}_2\text{O}$	32.22
Formate:		
11.	$\frac{1}{2} \text{HCO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{2} \text{HCOO}^- + \frac{1}{2} \text{H}_2\text{O}$	48.07

Reaction number	Half reaction	$\Delta G^\circ (W),^b$ kJ per electron equivalent
Glucose:		
12.	$\frac{1}{4} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{24} \text{C}_6\text{H}_{12}\text{O}_6 + \frac{1}{4} \text{H}_2\text{O}$	41.96
Carbohydrate (cellulose, starch, sugars):		
13.	$\frac{1}{4} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{4} \text{CH}_2\text{O} + \frac{1}{4} \text{H}_2\text{O}$	41.84
Methanol:		
14.	$\frac{1}{6} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{6} \text{CH}_3\text{OH} + \frac{1}{6} \text{H}_2\text{O}$	37.51
Pyruvate:		
15.	$\frac{1}{3} \text{CO}_2 + \frac{1}{10} \text{HCO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{10} \text{CH}_3\text{COCOO}^- + \frac{2}{3} \text{H}_2\text{O}$	35.78
Ethanol:		
16.	$\frac{1}{6} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{12} \text{CH}_3\text{CH}_2\text{OH} + \frac{1}{4} \text{H}_2\text{O}$	31.79
Propionate:		
17.	$\frac{1}{7} \text{CO}_2 + \frac{1}{14} \text{HCO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{14} \text{CH}_3\text{CH}_2\text{COO}^- + \frac{5}{14} \text{H}_2\text{O}$	27.91
Acetate:		
18.	$\frac{1}{8} \text{CO}_2 + \frac{1}{8} \text{HCO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{8} \text{CH}_3\text{COO}^- + \frac{3}{8} \text{H}_2\text{O}$	27.68
Grease (fats and oils):		
19.	$\frac{4}{23} \text{CO}_2 + \text{H}^+ + \text{e}^- = \frac{1}{46} \text{C}_8\text{H}_{16}\text{O} + \frac{15}{46} \text{H}_2\text{O}$	27.61
<i>Inorganic donors (autotrophic reactions):</i>		
20.	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	-74.40
21.	$\frac{1}{2} \text{NO}_3^- + \text{H}^+ + \text{e}^- = \frac{1}{2} \text{NO}_2^- + \frac{1}{2} \text{H}_2\text{O}$	-40.15
22.	$\frac{1}{8} \text{NO}_3^- + \frac{5}{4} \text{H}^+ + \text{e}^- = \frac{1}{8} \text{NH}_4^+ + \frac{3}{8} \text{H}_2\text{O}$	-34.50
23.	$\frac{1}{6} \text{NO}_2^- + \frac{4}{3} \text{H}^+ + \text{e}^- = \frac{1}{6} \text{NH}_4^+ + \frac{1}{3} \text{H}_2\text{O}$	-32.62
24.	$\frac{1}{6} \text{SO}_4^{2-} + \frac{4}{3} \text{H}^+ + \text{e}^- = \frac{1}{6} \text{S} + \frac{2}{3} \text{H}_2\text{O}$	19.48
25.	$\frac{1}{8} \text{SO}_4^{2-} + \frac{19}{16} \text{H}^+ + \text{e}^- = \frac{1}{16} \text{H}_2\text{S} + \frac{1}{16} \text{HS}^- + \frac{1}{2} \text{H}_2\text{O}$	21.28
26.	$\frac{1}{4} \text{SO}_4^{2-} + \frac{5}{4} \text{H}^+ + \text{e}^- = \frac{1}{8} \text{S}_2\text{O}_3^{2-} + \frac{5}{8} \text{H}_2\text{O}$	21.30
27.	$\frac{1}{6} \text{N}_2 + \frac{4}{3} \text{H}^+ + \text{e}^- = \frac{1}{3} \text{NH}_4^+$	27.47
28.	$\text{H}^+ + \text{e}^- = \frac{1}{2} \text{H}_2$	40.46
29.	$\frac{1}{2} \text{SO}_4^{2-} + \text{H}^+ + \text{e}^- = \text{SO}_3^{2-} + \text{H}_2\text{O}$	44.33

^aAdapted from McCarty (1975) and Sawyer et al. (1994).

^bReactants and products at unit activity except $[\text{H}^+] = 10^{-7}$.

Some standard half-cell potentials of biological interest

Half Cell	n^a	E'_0 (volts) ^{b,c}
acetate + CO ₂ + 2H ⁺ /pyruvate + H ₂ O	2	-0.70
succinate + CO ₂ + 2H ⁺ /α-ketoglutarate + H ₂ O	2	-0.67
acetate + 2H ⁺ /acetaldehyde + H ₂ O	2	-0.60
chlorophyll: P _I ⁺ /P _I ^{*d}	1	-0.6
3-P-glycerate + 2H ⁺ /glyceraldehyde-3-P + H ₂ O	2	-0.55
ferredoxin ox/red	1	-0.43
2H ⁺ /H ₂	2	-0.42
H ⁺ + CO ₂ /formate	2	-0.42
acetyl CoA + 2H ⁺ /acetaldehyde + CoASH	2	-0.41
CO ₂ + pyruvate + 2H ⁺ /malate + H ₂ O	2	-0.33
NAD(P) ⁺ + 2H ⁺ /NAD(P)H + H ⁺	2	-0.32
lipoate _{ox} + 2H ⁺ /lipoate _{red}	2	-0.29
1,3-diP-glycerate + 2H ⁺ /glyceraldehyde-3-P + P _i ^e	2	-0.29

acetoacetate + 2H ⁺ /β-hydroxybutyrate	2	-0.27
S + 2H ⁺ /H ₂ S	2	-0.23
chlorophyll: P _{II} ⁺ /P _{II} ^{*f}	1	-0.2
acetaldehyde + 2H ⁺ /ethanol	2	-0.20
pyruvate + 2H ⁺ /lactate	2	-0.19
FAD (flavin adenine dinucleotide) + 2H ⁺ /FADH ₂ (free)	2	-0.18 ^g
oxaloacetate + 2H ⁺ /malate	2	-0.17
α-ketoglutarate + NH ₄ ⁺ + 2H ⁺ /glutamate + H ₂ O	2	-0.14
pyruvate + NH ₄ ⁺ + 2H ⁺ /alanine + H ₂ O	2	-0.13
standard hydrogen half cell (2H ⁺ /H ₂)	2	<i>E</i> ₀ = 0.00
methylene blue ox/red	2	0.01
fumarate + 2H ⁺ /succinate	2	0.03
cytochrome <i>b</i> (Fe ³⁺ /Fe ²⁺)	1	0.06
ubiquinone ox/red	2	0.10
Cu ²⁺ /Cu ⁺	1	0.15
hemoglobin (Fe ³⁺ /Fe ²⁺)	1	0.17
cytochrome <i>c</i> (Fe ³⁺ /Fe ²⁺)	1	0.22
cytochrome <i>a</i> (Fe ³⁺ /Fe ²⁺)	1	0.29
2H ⁺ + O ₂ /H ₂ O ₂	2	0.30
chlorophyll: P _I ⁺ /P _I ⁰	1	0.4
NO ₃ ⁻ + 2H ⁺ /NO ₂ ⁻ + H ₂ O	2	0.42
SO ₄ ²⁻ + 2H ⁺ /SO ₃ ²⁻ + H ₂ O	2	0.48
Fe ³⁺ /Fe ²⁺	1	0.77
2H ⁺ + 1/2 O ₂ /H ₂ O	2	0.82
chlorophyll: P _{II} ⁺ /P _{II} ⁰	1	0.9

^a*n* is the number of transferred electrons.

^bFor a 2*e*⁻ reaction, Δ*E*'₀ of 0.10 volt corresponds to Δ*G*'₀ of -4.6 kcal/mole.

^cDetermined at pH = 7 and 25°C, relative to the standard hydrogen half cell (pH = 0).

^dChlorophyll at the photoreactive center of photosystem I in photosynthesis. P_I^{*}, P_I⁺, and P_I⁰ represent the excited, the electron-deficient, and the ground state forms, respectively, of the pigment molecule. See Chapter 12.

^eP_i represents inorganic phosphate, HPO₄²⁻.

^fChlorophyll at the photoreactive center of photosystem II in eucaryotic photosynthesis. P_{II}^{*}, P_{II}⁺, and P_{II}⁰ represent the excited, the electron-deficient, and the ground-state forms, respectively, of the pigment. See Chapter 12.

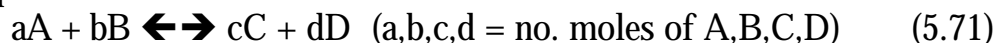
^gThis value is for the free coenzyme. Different flavoproteins, carrying bound FAD (Chapter 11), vary in *E*'₀ from approximately 0.0 to 0.3 volt.

(c) Both chemotrophs and phototrophs obtain energy from redox reactions. Chemotrophs require an environmental source of high-energy electrons (e.g., an organic molecule) and an acceptor to which

Thermodynamics & Bioenergetics

10/21/03

Consider the relationship between standard free energy change (ΔG°) and the equilibrium constant for a chemical reaction:



$$K'_{\text{eq}}(@ \text{pH}=7) = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (11)$$

$$\Delta G' = \Delta G^{\circ} + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (5.7.2)$$

Free energy change = standard free energy change + f(constituent concs)

If we allow reaction (5.71) to proceed toward equilibrium, free energy change will **decrease** during the drive to equilibrium. In the drive toward equilibrium the reaction will do work at constant temp. and pressure. When the system reaches equilibrium, no further net chemical change will occur, and $\Delta G' = 0$.

At equilibrium, $\Delta G' = 0$, and

$$0 = \Delta G^{\circ} + RT \ln K'_{\text{eq}} \quad (13)$$

ΔG° = Standard Free Energy [temp 25°C, 298 K; pressure 1 atm, concentration of reactants and products = 1 molal concentration (use 1 Molar)]. $R = 1.98 \text{ cal./K} - \text{mole}$.

In addition, biochemists use two **non-standard** conditions: (1) pH=7, and (2) water concentration assumed constant]. By convention, both H^+ ion concentration and water concentration are left out of the equilibrium expression (11) and are included in the value of K'_{eq} for any reaction in which they appear. Then ΔG° is shown as ΔG° .

At equilibrium, $\Delta G' = 0$, and expression becomes:

$$\Delta G^{\circ} = - RT \ln K'_{\text{eq}} \quad (14)$$

$\Delta G' = \Delta G^{\circ}$ only when all reactants and products are present at 1.0 M.

Now, how about the concentrations of reactants and products in a human cell?

Sample calculation:

Given: Enzyme phosphoglucosmutase, catalyzes reaction
Glucose-1-phosphate \leftrightarrow glucose-6-phosphate
Start with 0.020 M G-1-P, add the enzyme, and allow reaction to proceed, the final equilibrium mixture will have 0.001 M G-1-P and 0.019 M G-6-P at 25C and pH=7.

Calculate: equilibrium constant and Standard Free Energy change

$$K_{eq} = \frac{G-6-P}{G-1-P} = \frac{0.019}{0.001} = 19$$

The Standard Free Energy change would be:

$$\begin{aligned}\Delta G'_{o} &= -RT \ln K_{eq} \\ &= -1.987 \text{ cal/mol} \times 298 \text{ K} (\ln 19) \\ \Delta G'_{o} &= -1743 \text{ cal/mol}\end{aligned}$$

Standard Free Energy change of a chemical reaction is the Difference between sum of free energies of products and sum of free energies of reactants (all in standard state), i.e., conc. of 1 Molar, temp 25C, pressure 1 atm.

Each chemical compound has a characteristic, intrinsic free energy by virtue of its molecular structure. Standard free energy change $\Delta G'_{o}$ can be expressed as:

$$\Delta G'_{o} = \sum G^{\circ}_{\text{products}} - \sum G^{\circ}_{\text{reactants}} \quad (15)$$

For reaction (5.71) $\Delta G'_{o} = (cG^{\circ}_c + dG^{\circ}_D) - (aG^{\circ}_A + bG^{\circ}_B) \quad (16)$

Example: Enzyme Fumarase - Fumarate to Malate

$$\begin{aligned}\text{Fumarate} + \text{H}_2\text{O} &= \text{Malate} \\ \Delta G'_{o} &= \Delta G'_{o}_{\text{malate}} - (\Delta G'_{o}_{\text{fumarate}} + \Delta G'_{o}_{\text{H}_2\text{O}}) \\ &= -201.98 - (-144.41 - 56.69) \\ &= -0.88 \text{ kcal/mol}\end{aligned}$$