Chapter 2

Stoichiometry and Energetics

Problems According to Major Subject Addressed

Basic Half-Reactions
6, 7

Energy Reactions
1, 3, 4

$f_s°$ from Energetics
2, 5, 9, 10, 11, 12, 13

Stoichiometry of Overall Reactions
8, 14, 15, 16, 17

2.1

Case	Electron Donor	Electron Acceptor	Answer	$\Delta G_r^{o'}$, kJ/e⁻eq
a.	Acetate	carbon dioxide (methanogenesis)	Yes	23,5-27,4 = -3,9
b.	Acetate	Fe^{3+} (Reduction to Fe_2^{+})	Yes	-74,3 -27,4 = -101,7
c.	Acetate	H^+ (reduction to H_2)	No	39.9 -27,4 = +12,5
d.	Glucose	H^+ (reduction to H_2)	YES	39,9 - 41,35 = -1,45
e.	H_2	carbon dioxide (methanogenesis)	Yes	23,5 - 39.9 = -16.4
f.	H_2	nitrate (denitrification to N_2)	yes	-72,2 - 39,9 = -112,1
g.	S (oxidized to sulfate)	NO_3^- (denitrification to N_2)	Yes	-72,2 - 19,2 = -91,4
h.	CH_4	NO_3^- (denitrification to N_2)	Yes	-72,2 - 23.5 = -95,7
i.	NH_4^+ (oxidation to NO_2^-)	SO_4^{2-} (reduction to H_2S + HS^-)	No	35,1 - 20.85 = +14.25

2.2

Case	Donor	Acceptor	N-source	ΔG_r	ΔG_p	ΔG_{pc}	A	f_s^o
a	Ethanol	O_2	NH_4^+	-109,9	3.9	18,8	0,57	0.64
b	Ethanol	O_2	NO_3^-	-109,9	3.9	13,4	0,44	0,70
c	Ethanol	SO_4^{2-}	NH_4^+	~~-109,9~~ -10,3	3,9	18.8	6,1	0,14
d	Ethanol	~~SO_4^{2-}~~ CO_2	NH_4^+	-7,65	3.9	18,8	8.25	0.11
e	Propionate	CO_2	NH_4^+	-4,1	7,5	18,8	17,8	0.05
f	$S \to SO_4^{2-}$	NO_3^-	NH_4^+	-91,4	113,8	18,8	4,0	0,20
g	$NH_4^+ \to NO_2^-$	O_2	NH_4^+	-45,8	113,8	18,8	8.0	0.11

2.3

(a) $\Delta G_d^\circ = \frac{1}{4}\Delta G^\circ_{butyrate} + \frac{1}{4}\Delta G^\circ_{HCO_3^-} + \frac{1}{4}\Delta G^\circ_{H_2O} - \frac{1}{2}\Delta G^\circ_{acetate} - \frac{1}{4}\Delta G^\circ CO_2 - \Delta G^\circ_{H^+} - \Delta G^\circ_{e^-}$

$= \frac{1}{4}(-352.63) + \frac{1}{4}(-586.85) + \frac{1}{4}(-237.18)$
$\quad -\frac{1}{2}(-369.41) - \frac{1}{4}(-386.02) - 0 - 0$

$= -88.16 - 146.71 - 59.30 + 184.71 + 96.51 - 0 - 0$
$= -12.95$ kjoule/e⁻ eq

$\Delta G_a^\circ = \frac{1}{2}\Delta G^\circ_{H_2} - \Delta G^\circ_{H^+} - \Delta G^\circ_{e^-}$
$= \frac{1}{2}(0) - 0 - 0 = 0$ kjoule/e⁻ eq

$\Delta G_r^\circ = (-12.95) - 0 = -12.95$ kj/e⁻ eq.

(b) pH = 7. $\Delta G^\circ_{H^+} = -39.87$ kj/mole now.
So, $\Delta G_d^{\circ\prime} = -12.95 - (-39.87) = +26.92$ kj/e⁻ eq
$\Delta G_a^{\circ\prime} = 0 - (-39.87) = 39.87$ kj/e⁻ eq
$\Delta G_r' = (+26.92) - (39.87) = -12.95$ kj/e⁻ eq.

(c) $\Delta G_r' = -\Delta G^\circ + RT\ln Q$

Rxn: $\frac{1}{2}CH_3COO^- + \frac{1}{4}CO_2 + \frac{1}{2}H_2 = \frac{1}{4}CH_3CH_2CH_2COO^- + \frac{1}{4}HCO_3^- + \frac{1}{4}H_2O$

$$\Delta G_r' = -12.95 + 8.31\times10^{-3}\ \text{kj/°K-mol} \times 293\,K \ln\frac{[10^{-2}]^{1/4}[1]^{1/4}[10^{-1}]^{1/4}}{[10^{-3}]^{1/2}[0.3]^{1/4}[10^{-6}]^{1/2}}$$

$$= -12.95 + 2.43\ln\frac{3.16\times10^{-1}\times1\times5.62\times10^{-1}}{3.16\times10^{-2}\times7.4\times10^{-1}\times10^{-3}}$$

$= -12.95 + 2.43\times4.33 = -24$ kj/e⁻ eq.

All ΔG_r values are negative, and bacteria should gain energy.

2.4

ΔG_r	Ethanol to CH_4	$23.53 - 31.18 = -7.65$ kJ
	Acetate + SO_4^{2-}	$20.85 - 27.40 = -6.55$ kJ

Ethanol to CH_4 gives more cell production per equivalent because more energy is released.

2.5

$$A = -\frac{\Delta G_s}{k^2 \Delta G_r}$$

$$\Delta G_s = \Delta G_c - \Delta G_d = 53.92 - 27.34 = 26.58 \text{ kJ/eq.}$$

$$\Delta G_r = \Delta G_a - \Delta G_d = 20.85 - 27.34 = -6.49 \text{ kJ/eq.}$$

$$A = -\frac{26.58}{(0.6)^2(-6.49)} = 11.38$$

$$F_s = \frac{1}{1+A} = \frac{1}{1+11.38} = 0.081 \frac{\text{eq. cells}}{\text{eq. donor}}$$

$$Y = 0.081 \frac{\text{eq. cells}}{\text{eq. donor}} \times \frac{\text{eq. donor}}{\frac{1}{30}(121)\text{ g donor}} \times \frac{\frac{1}{20}(113)\text{ g cells}}{\text{eq. cells}} = 0.11 \frac{\text{g cells}}{\text{g benzoate}}$$

2.6

One eq. lactate ≑ one eq. O_2 ≑ 8 g O_2

$$F_e = 1 - F_s = 1 - 0.4 = 0.6 \quad \text{(Fraction oxidized)}$$

$$\therefore O_2 \text{ required} = F_e(8) = 0.6(8) = 4.8 \text{ g } O_2$$

2.7

(a) $\frac{1}{24}CH_3CH_2CH_2CHNH_2COO^- + \frac{3}{8}H_2O \rightarrow$

$\frac{1}{24}NH_4^+ + \frac{1}{24}HCO_3^- + \frac{1}{6}CO_2 + \frac{23}{24}H^+ + e^-$

or

$\frac{1}{24}CH_3CH_2CH_2CHNH_2COO^- + \frac{5}{12}H_2O \rightarrow$

$\frac{1}{24}NH_4^+ + \frac{1}{12}HCO_3^- + \frac{1}{8}CO_2 + H^+ + e^-$

(b) $\frac{1}{6}Cl^- + \frac{1}{2}H_2O \rightarrow \frac{1}{6}ClO_3^- + H^+ + e^-$

2.8

$\frac{1}{6} CH_3OH + \ldots\ldots \rightarrow \frac{1}{6} CO_2 + \ldots\ldots + e^-$

$0.3(\frac{1}{28} NO_3^-) + \ldots\ldots 0.3e^- \rightarrow 0.3(\frac{1}{28}) C_5H_7O_2N + \ldots\ldots$

$0.7(\frac{1}{5} NO_3^-) + \ldots\ldots 0.7e^- \rightarrow 0.7(\frac{1}{10}) N_2 + \ldots\ldots$

$\frac{1}{6} CH_3OH + [0.3(\frac{1}{28}) + 0.7(\frac{1}{5})] NO_3^- + \ldots \rightarrow 0.07 N_2 + \ldots$

$\frac{1}{6}(32)$ $\quad 0.1507\ (14)$

$5.33\ g\ CH_3OH$ $\quad 2.11\ g\ NO_3^- - N$

CH_3OH minimum $= \frac{5.33}{2.11}(84) = \underline{\underline{212}}\ mg/l$

2.9

$f_s^\circ = 0.16 = \frac{1}{1+A} \Longrightarrow A = 5.25 \frac{e^- eq\ acceptor}{e^- eq\ cells}$

$$A = -\frac{\Delta G_p/k^m + \Delta G_{pc}/k}{k \Delta G_r}$$

$\Delta G_{pc} = +18.8\ kJ/e^- eq$ (NH_4^+ as N source)

$\Delta G_p = 35.09 - ~~53.55~~\ 27.4$ (Acetate as C source) $= 7.69\ kJ/e^- eq$

$m = +1$ as $\Delta G_p > 0$

$\Delta G_r = -53.55\ (PCE) - 27.4\ (Ac) = -80.95\ kJ/e^- eq$

$$5.25 = -\frac{7.69/k + 18.8/k}{k(-80.95)} = \frac{26.49}{80.95} \cdot \frac{1}{k^2}$$

$k^2 = 0.062$

$k = 0.25$ (a low value)

2.10 In general, $\Delta G_r = \Delta G_a - \Delta G_d$ (kJ/e⁻ eq)

$\Delta G_p = 35.09 - \Delta G_c$ (= 113.8 kJ/e⁻ eq for CO_2)

ΔG_{pc} = ~~18.8~~ 13.4 for NO_3^-, 14.5 for NO_2^-, 16.4 for N_2, & 18.8 for NH_4^+

$$A = \frac{\Delta G_p / k^m + \Delta G_{pc}/k}{-k \Delta G_r}$$

$$f_s^0 = \frac{1}{1+A} \quad \text{(in e}^- \text{ cells/e}^- \text{ donor)}$$

$$Y = f_s^0 \frac{e^- \text{cells}}{e^-} \cdot \frac{113 \text{ g cells}}{20 + n \text{ e}^- \text{ cells}} \cdot \frac{\text{e}^- \text{ donor}}{8 \text{ g BOD}_L} \quad \left(\frac{\text{g VSS}}{\text{g BOD}_L}\right)$$

$n = 0$ for NH_4^+, 8 for NO_3^-, 6 for NO_2^-, and 3 for N_2

Donor	Acceptor	C-Source	N-Source	ΔG_r	ΔG_p	ΔG_{pc}	A	f_s^0	Y
Acetate (ΔG_r^0 = 27.4 kJ/e⁻ eq)	O_2 (−78.72)	Acetate (ΔG_c = 27.4)	NH_4^+	−106.1	7.7	18.8	0.69	0.59	0.42
			NO_3^-	↓	↓	13.4	0.55	0.64	0.33
			NO_2^-			14.5	0.58	0.63	0.34
			N_2			16.4	0.63	0.61	0.38

2.11 (Same pattern as 2.10)

Donor	Acceptor	C-Source	N-Source	ΔG_r	ΔG_p	ΔG_{pc}	A	f_s^0	Y
glucose (41.35)	O_2 (−78.72)	Glucose (41.35)	NH_4	−120.1	−6.3	18.8	0.38	0.72	0.51
↓	↓	↓	NO_3^-	↓	↓	13.4	0.26	0.80	0.40
			NO_2^-			14.5	0.28	0.78	0.42
			N_2			16.4	0.33	0.75	0.46

2.12 For CO_2 as C-source (normal)

$\Delta G_r = -78.72 - (-35.1) = -43.6$ kJ/e⁻eq

$\Delta G_p = 35.09 - (-78.72) = 113.8$ kJ/e⁻eq

$\Delta G_{pc} = 18.8$ kJ/e⁻eq.

$$A = \frac{113.8/0.6 + 18.8/0.6}{-0.6(-43.6)} = 8.45 \frac{e^- \text{ acceptor}}{e^- \text{ cells}}$$

$$f_s^o = \frac{1}{1+8.45} = 0.11 \frac{e^- \text{ cells}}{e^- \text{ donor}}$$

$$Y = 0.11 \frac{e^- \text{ cells}}{e^- \text{ donor}} \cdot \frac{113 \text{ g cells}}{20 e^- \text{ cells}} \cdot \frac{8 e^- \text{ donor}}{14 \text{ g } NH_4^+\text{-N}} = 0.34 \frac{\text{g cells}}{\text{g } NH_4^+\text{-N}}$$

For Acetate, the change is to

$\Delta G_p = 35.09 - 27.4 = 7.7$ kJ/e⁻eq

$$A = \frac{7.7/0.6 + 18.8/0.6}{-(0.6)(-43.6)} = 1.7 \frac{e^- \text{ ~~donor~~ acceptor}}{e^- \text{ cells}}$$

$$f_s^o = \frac{1}{1+1.7} = 0.37 \frac{e^- \text{ cells}}{e^- \text{ donor}}$$

$$Y = 0.37 \cdot \frac{113}{20} \times \frac{8}{14} = 1.2 \text{ g cells/g } NH_4^+\text{-N}$$

A big potential advantage!

2.13 $\Delta G_d = 39.9$ kJ/e⁻ eq (H_2)

$\Delta G_a = -78.7$ for O_2 or $+20.85$ for SO_4^{2-}

$\Delta G_p = 113.8$ (autotrophy)

$\Delta G_{pc} = 18.8$

$$A = \frac{113.8/0.6 + 18.8/0.6}{-0.6(\Delta G_r)} = 368.3/-\Delta G_r$$

For O_2 as acceptor, $\Delta G_r = -39.9 + (-78.7) = -118.6$ kJ/e⁻ eq

$A = 3.11$

For SO_4^{2-} as acceptor, $\Delta G_r = -39.9 + (+20.85) = 19.05$ kJ/e⁻ eq

$A = 19.3$

Then $f_s^0 = \frac{1}{1+A}$ = 0.24 for O_2

= 0.05 for SO_4^{2-}

$$Y = f_s^0 \cdot \frac{113 \text{ g cells}}{20 \text{ e}^- \text{ eq}} \cdot \frac{2 \text{ e}^- \text{ eq}}{2 \text{ g } H_2}$$

or = 1.38 g cells/g H_2 for O_2

= 0.28 g cells/g H_2 for SO_4^{2-}

2.14 $f_s^0 = 0.333$, $f_e^0 = 0.667$. Acetate/NO_3^-/NO_3^-

$$\frac{1}{8} CH_3COO^- + 0.145 H^+ + 0.145 NO_3^- \longrightarrow 0.156 H_2O + 0.065 CO_2 + 0.067 N_2 + 0.125 HCO_3^- + 0.0119 C_5H_7O_2N$$

2.15 $Cu(s)/O_2/CO_2/NH_4$: $f_s^\circ = 0.036$, $f_e^\circ = 0.964$

$$\tfrac{1}{2} Cu(s) + 0.241 O_2 + H^+ + 0.0018 NH_4^+ + 0.0018 HCO_3^- + 0.0072 CO_2 \longrightarrow \tfrac{1}{2} Cu^{2+} + 0.4982 H_2O + 0.0018 C_5H_7O_2N$$

2.16 $NH_4^+/O_2/CO_2/NH_4$ ($\to NO_2^-$) $f_s^\circ = 0.061$, $f_e^\circ = 0.939$

$$0.170 NH_4^+ + 0.0030 HCO_3^- + 0.0122 CO_2 + 0.235 O_2 \longrightarrow 0.416 H_2O + 0.1667 NO_2^- + 0.333 H^+ + 0.0030 C_5H_7O_2N$$

2.17 $CH_2Cl_2/O_2/CH_2Cl_2/NH_4^+$ $f_s^\circ = 0.31$ $f_e^\circ = 0.69$

$$0.25 CH_2Cl_2 + 0.0155 H_2O + 0.0155 NH_4^+ + 0.1725 O_2 + 0.0155 HCO_3^- \longrightarrow 0.5 H^+ + 0.0155 C_5H_7O_2N + 0.188 CO_2 + 0.5 Cl^-$$
