

## Chapter 2

### Stoichiometry and Energetics

#### Problems According to Major Subject Addressed

##### Basic Half-Reactions

6, 7

##### Energy Reactions

1, 3, 4

##### $f_r^\circ$ 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
a.	Acetate	carbon dioxide (methanogenesis)
b.	Acetate	Fe <sup>3+</sup> (Reduction to Fe <sup>2+</sup> )
c.	Acetate	H <sup>+</sup> (reduction to H <sub>2</sub> )
d.	Glucose	H <sup>+</sup> (reduction to H <sub>2</sub> )
e.	H <sub>2</sub>	carbon dioxide (methanogenesis)
f.	H <sub>2</sub>	nitrate (denitrification to N <sub>2</sub> )
g.	S (oxidized to sulfate)	NO <sub>3</sub> <sup>-</sup> (denitrification to N <sub>2</sub> )
h.	CH <sub>4</sub>	NO <sub>3</sub> <sup>-</sup> (denitrification to N <sub>2</sub> )
i.	NH <sub>4</sub> <sup>+</sup> (oxidation to NO <sub>2</sub> <sup>-</sup> )	SO <sub>4</sub> <sup>2-</sup> (reduction to H <sub>2</sub> S + HS <sup>-</sup> )

Answer

$\Delta G_r', \text{ kJ/e}^{-20}$

Yes

$23.5 - 27.4 = -3.9$

Yes

$-74.3 - 27.4 = -101.7$

No

$39.9 - 27.4 = +12.5$

Yes

$39.9 - 41.35 = -1.45$

Yes

$23.5 - 39.9 = -16.4$

Yes

$-72.2 - 39.9 = -112.1$

Yes

$-72.2 - 19.2 = -91.4$

Yes

$-72.2 - 23.5 = -95.7$

No

$35.1 - 20.85 = +14.25$

2.2

Case	Donor	Acceptor	N-source	$\Delta G_r$	$\Delta G_p$	$\Delta G_{pc}$	A	$f_s^0$
a	Ethanol	O <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	-109.9	3.9	18.8	0.57	0.64
b	Ethanol	O <sub>2</sub>	NO <sub>3</sub> <sup>-</sup>	-109.9	3.9	13.4	0.44	0.70
c	ethanol	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	<del>-109.9</del> -10.3	3.9	18.8	6.1	0.14
d	Ethanol	<del>SO<sub>4</sub><sup>2-</sup></del> CO <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	-71.65	3.9	18.8	8.25	0.11
e	Propionate	CO <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	-4.1	7.5	18.8	17.8	0.05
f	S → SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	-91.4	113.8	18.8	4.0	0.20
g	NH <sub>4</sub> <sup>+</sup> → NO <sub>2</sub> <sup>-</sup>	O <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	-45.8	113.8	18.8	8.0	0.11

2.3

$$\begin{aligned}
 (a) \Delta G_d^\circ &= \frac{1}{4} \Delta G_{butyrate}^\circ + \frac{1}{4} \Delta G_{HCO_3^-}^\circ + \frac{1}{4} \Delta G_{H_2O}^\circ - \frac{1}{2} \Delta G_{acetate}^\circ - \frac{1}{4} \Delta G_{CO_2}^\circ - \Delta G_{H^+}^\circ - \Delta G_{e^-}^\circ \\
 &= \frac{1}{4} (-352.63) + \frac{1}{4} (-586.85) + \frac{1}{4} (-237.18) \\
 &\quad - \frac{1}{2} (-369.41) - \frac{1}{4} (-386.02) - 0 - 0 \\
 &= -88.16 - 146.71 - 59.30 + 184.71 + 96.51 - 0 - 0 \\
 &= -12.95 \text{ kJoule/e}^- \text{ eq}
 \end{aligned}$$

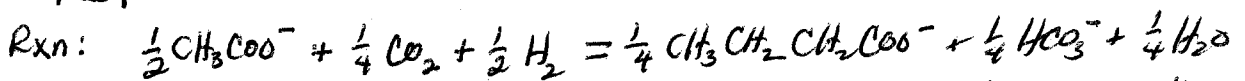
$$\begin{aligned}
 \Delta G_a^\circ &= \frac{1}{2} \Delta G_{H_2}^\circ - \Delta G_{H^+}^\circ - \Delta G_{e^-}^\circ \\
 &= \frac{1}{2} (0) - 0 - 0 = 0 \text{ kJoule/e}^- \text{ eq}
 \end{aligned}$$

$$\Delta G_r^\circ = (-12.95) - 0 = -12.95 \text{ kJ/e}^- \text{ eq}$$

(b)  $pH = 7$ .  $\Delta G_{H^+}^\circ = -39.87 \text{ kJ/mole now}$ .

$$\begin{aligned}
 \text{So, } \Delta G_d^\circ &= -12.95 - (-39.87) = +26.92 \text{ kJ/e}^- \text{ eq} \\
 \Delta G_a^\circ &= 0 - (-39.87) = 39.87 \text{ kJ/e}^- \text{ eq} \\
 \Delta G_r^\circ &= (+26.92) - (39.87) = -12.95 \text{ kJ/e}^- \text{ eq}
 \end{aligned}$$

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



$$\begin{aligned}
 \Delta G_r' &= -12.95 + 8.31 \times 10^{-3} \text{ kJ/K-mol} \times 293 \text{ K} \ln \frac{[10^{-2}]^4 [1]^4 [10^{-1}]^4}{[10^{-3}]^2 [0.3]^4 [10^{-6}]^{1/2}} \\
 &= -12.95 + 2.43 \ln \frac{3.16 \times 10^{-1} \times 5.62 \times 10^{-1}}{3.16 \times 10^{-2} \times 7.4 \times 10^{-1} \times 10^{-3}} \\
 &= -12.95 + 2.43 \times 4.33 = -2.4 \text{ kJ/e}^- \text{ eq}
 \end{aligned}$$

All  $\Delta G_r'$  values are negative, and bacteria should gain energy.

2.4

$\Delta G_r$	Ethanol to City	$23.53 - 31.18 = -7.65 \text{ kJ}$
	Acetate + $\text{SO}_4^{2-}$	$20.85 - 27.40 = -6.55 \text{ kJ}$

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

2.5

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

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

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

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

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

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

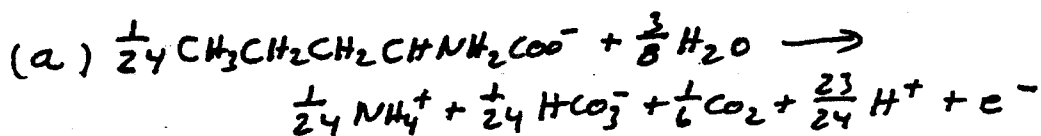
2.6

One eq. lactate  $\neq$  one eq.  $\text{O}_2 \doteq 8 \text{ g O}_2$

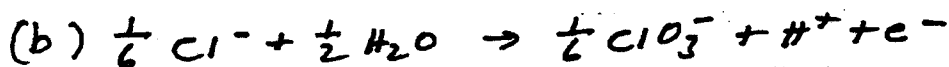
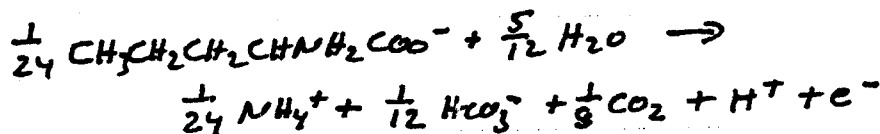
$$F_c = 1 - F_s = 1 - 0.4 = 0.6 \quad (\text{Fraction oxidized})$$

$$\therefore \text{O}_2 \text{ required} = F_c (8) = 0.6 (8) = \underline{\underline{4.8 \text{ g O}_2}}$$

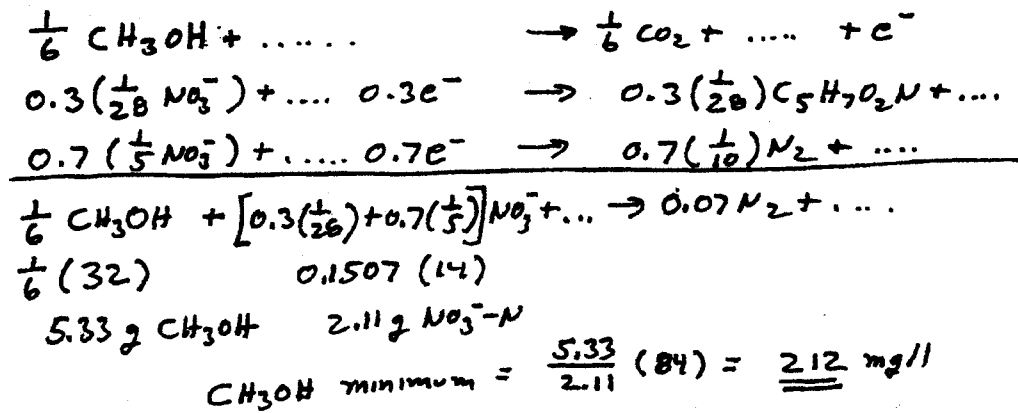
2.7



or



2.8



2.9

$$f_s^0 = 0.16 = \frac{1}{1+A} \Rightarrow A = 5.25 \frac{e^- \text{ eq acceptor}}{e^- \text{ eq cells}}$$

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

$$\Delta G_{pc} = +18.8 \text{ kJ/e}^- \text{ eq} \quad (\text{NH}_4^+ \text{ as N source})$$

$$\Delta G_{ps} = 35.09 - \cancel{53.55} 27.4 \text{ (Acetate as source)} = 7.69 \text{ kJ/e}^- \text{ eq}$$

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

$$\Delta G_r = -53.55 \text{ (PE)} - 27.4 \text{ (Ac)} = -80.95 \text{ kJ/e}^- \text{ eq}$$

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

$$k^2 = 0.062$$

$$k = 0.25 \quad (\text{a low value})$$

2.10 In general,  $\Delta G_r = \Delta G_a - \Delta G_d$  (kJ/e<sup>-</sup>eg)

$$\Delta G_p = 35.09 - \Delta G_c \quad (= 113.8 \text{ kJ/e}^- \text{ eg for CO}_2)$$

$$\Delta G_{pc} = \begin{matrix} 13.4 \\ \cancel{18.8} \end{matrix} \text{ for NO}_3^-, 14.5 \text{ for NO}_2^-, 16.4 \text{ for N}_2, \text{ \&18.8 for NH}_4^+$$

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

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

$$Y = f_s^0 \frac{\text{e}^- \text{ cells}}{\text{e}^-} \cdot \frac{113 \text{ g cells}}{20+n \text{ e}^- \text{ cells}} \cdot \frac{\text{e}^- \text{ donor}}{8 \text{ g BOD}_2} \quad \left( \frac{\text{g VSS}}{\text{g BOD}_2} \right)$$

$n = 0$  for NH<sub>4</sub><sup>+</sup>, 8 for NO<sub>3</sub><sup>-</sup>, 6 for NO<sub>2</sub><sup>-</sup>, and 3 for N<sub>2</sub>

Donor -	Acceptor	C-Source	N-Source	$\Delta G_r$	$\Delta G_p$	$\Delta G_{pc}$	A	$f_s^0$	Y
Acetate ( $\Delta G_r = 27.4$ kJ/e <sup>-</sup> eg)	O <sub>2</sub> (-78.72)	Acetate ( $\Delta G_c = 27.4$ )	NH <sub>4</sub> <sup>+</sup>	-106.1	7.7	18.8	0.69	0.59	0.42
			NO <sub>3</sub> <sup>-</sup>	↓	↓	13.4	0.55	0.64	0.33
			NO <sub>2</sub> <sup>-</sup>	↓	↓	14.5	0.58	0.63	0.34
			N <sub>2</sub>	↓	↓	16.4	0.63	0.61	0.38

2.11 (Same pattern as 2.10)

Donor	Acceptor	C-Source	N-Source	$\Delta G_r$	$\Delta G_p$	$\Delta G_{pc}$	A	$f_s^0$	Y
glucose (4635)	O <sub>2</sub> (-78.72)	Glucose ( <del>4635</del> (41,35))	NH <sub>4</sub>	-120.1	-4.3	18.8	0.38	0.72	0.57
			NO <sub>3</sub> <sup>-</sup>	↓	↓	13.4	0.26	0.80	0.40
			NO <sub>2</sub> <sup>-</sup>	↓	↓	14.5	0.28	0.78	0.42
			N <sub>2</sub>	↓	↓	16.4	0.33	0.75	0.46

2.12

For  $\text{CO}_2$  as C-source (normal)

$$\Delta G_r = -78,72 - (-35,1) = -43,6 \text{ kJ/e}^- \text{ eq}$$

$$\Delta G_p = 35,09 - (-78,72) = 113,8 \text{ kJ/e}^- \text{ eq}$$

$$\Delta G_{pc} = 18,8 \text{ kJ/e}^- \text{ eq}$$

$$A = \frac{113,8/0,6 + 18,8/0,6}{-0,6(-43,6)} = 8,45 \frac{\text{e}^- \text{ acceptor}}{\text{e}^- \text{ cells}}$$

$$f_6^0 = \frac{1}{1+8,45} = 0,11 \frac{\text{e}^- \text{ cells}}{\text{e}^- \text{ donor}}$$

$$Y = 0,11 \frac{\text{e}^- \text{ cells}}{\text{e}^- \text{ donor}} \cdot \frac{113 \text{ g cells}}{200 \text{ e}^- \text{ cells}} \cdot \frac{8 \text{ e}^- \text{ donor}}{14 \text{ g NH}_4^+ \text{ - N}} = 0,34 \frac{\text{g cells}}{\text{g NH}_4^+ \text{ - N}}$$

For Acetate, the charge is 4

$$\Delta G_p = 35,09 - 27,4 = 7,7 \text{ kJ/e}^- \text{ eq}$$

$$A = \frac{7,7/0,6 + 18,8/0,6}{-10,6(-43,6)} = 1,7 \frac{\text{e}^- \text{ donor acceptor}}{\text{e}^- \text{ cells}}$$

$$f_8^0 = \frac{1}{1+1,7} = 0,37 \frac{\text{e}^- \text{ cells}}{\text{e}^- \text{ donor}}$$

$$Y = 0,37 \cdot \frac{113}{20} \cdot \frac{8}{14} = 1,2 \frac{\text{g cells}}{\text{g NH}_4^+ \text{ - N}}$$

A big potential advantage!

2.13

$$\Delta G_d = 39.9 \text{ kJ/e}^- \text{ eq } (\text{H}_2)$$

$$\Delta G_a = -78.7 \text{ for } \text{O}_2 \text{ or } +20.85 \text{ for } \text{SO}_4^{2-}$$

$$\Delta G_p = 113.8 \text{ (autotrophy)}$$

$$\Delta G_{pc} = 18.8$$

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

$$\text{For } \text{O}_2 \text{ as acceptor, } \Delta G_r = -39.9 + (-78.7) = -118.6 \text{ kJ/e}^- \text{ eq}$$

$$A = 3.11$$

$$\text{For } \text{SO}_4^{2-} \text{ as acceptor, } \Delta G_r = -39.9 + (+20.85) = -19.05 \text{ kJ/e}^- \text{ eq}$$

$$A = 19.3$$

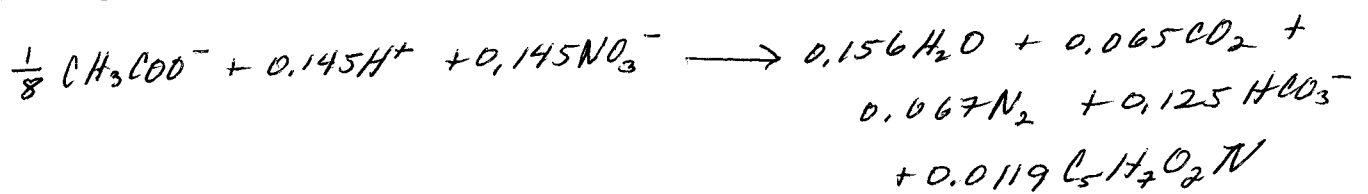
$$\text{Then } f_s^0 = \frac{1}{1+A} = 0.24 \text{ for } \text{O}_2$$

$$= 0.05 \text{ for } \text{SO}_4^{2-}$$

$$Y = f_s^0 \cdot \frac{113 \text{ g cells}}{20 \text{ e}^- \text{ eq}} \cdot \frac{2 \text{ e}^- \text{ eq}}{2 \text{ g H}_2}$$

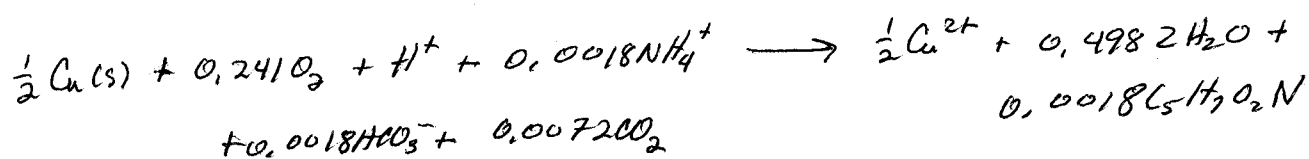
$$= 1.38 \text{ g cells/g H}_2 \text{ for } \text{O}_2$$

$$= 0.28 \text{ g cells/g H}_2 \text{ for } \text{SO}_4^{2-}$$

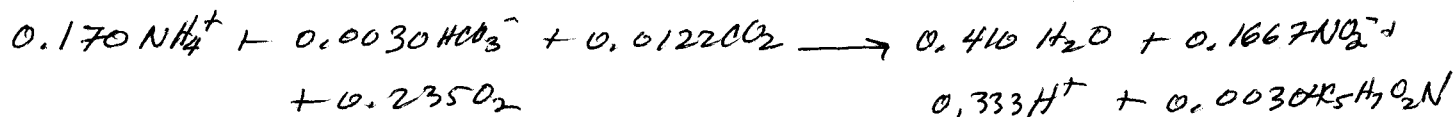
2.14  $f_s^0 = 0.333$ ,  $f_o^0 = 0.667$ . Acetate/ $\text{NO}_3^-$ / $\text{NO}_3^-$ 



2.15  $\text{Cu(s)}/\text{O}_2/\text{CO}_2/\text{NH}_4$  :  $f_s^\circ = 0.034$  ,  $f_e^\circ = 0.964$



2.16  $\text{NH}_4^+/\text{O}_2/\text{CO}_2/\text{NH}_4$   $f_s^\circ = 0.061$  ,  $f_e^\circ = 0.939$   
 $\hookrightarrow \text{NO}_2^-$



2.17  $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{CO}_2/\text{NH}_4^+$   $f_s^\circ = 0.31$   $f_e^\circ = 0.69$

