

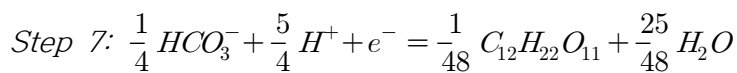
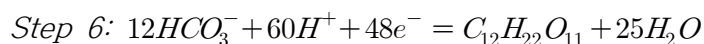
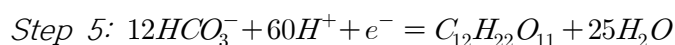
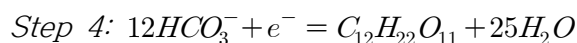
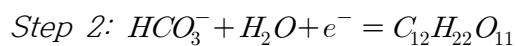
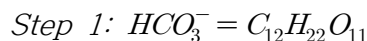
Homework #2 - SOLUTIONS

*** Answer the following questions. Be sure to clearly show the procedures to solve the problems.**

1. You want to develop an eco-friendly and cost-effective process for removal of nitrate (NO_3^-) from groundwater. Your plan is to supply molasses, a byproduct of sugar manufacturing, as an e^- donor to enhance denitrification in groundwater. Assuming that the molecular formula of molasses can be represented by $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (same as that for sugar), answer the following.

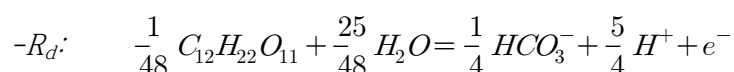
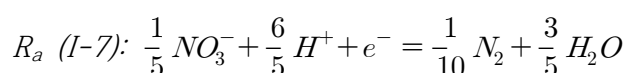
- 1) Write the electron donor half reaction, R_d , in an electron-equivalent form. Use HCO_3^- as an only form of an oxidized carbon species. (20 points)

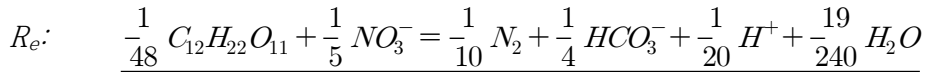
Solution)



- 2) Write the energy reaction, R_e , in an electron-equivalent form. How much grams of molasses are needed per g of $\text{NO}_3\text{-N}$ consumed for the energy reaction? (20 points)

Solution)



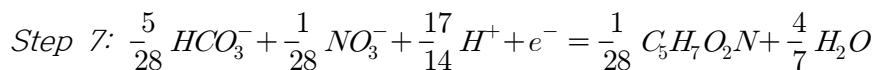
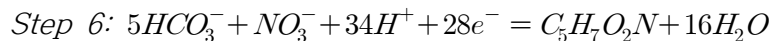
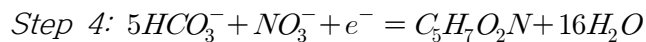
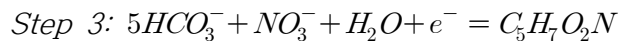
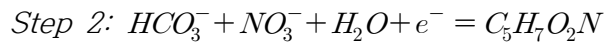


Molasses molecular weight: $12 \times 12 + 1 \times 22 + 16 \times 11 = 342$

$$g \text{ molasses needed}/g \text{ NO}_3\text{-N consumed} = \frac{\frac{1}{48} \text{ mole} \times 342 \text{ g molasses/mole}}{\frac{1}{5} \text{ mole} \times 14 \text{ g NO}_3\text{-N/mole}} = 2.54$$

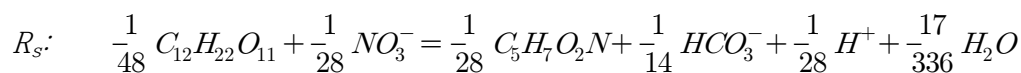
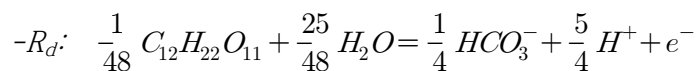
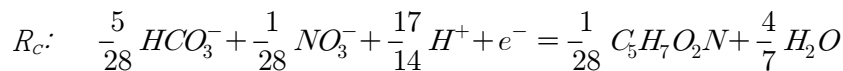
- 3) Write the cell formation half reaction, R_c , in an electron-equivalent form. Use the cell formula of $C_5H_7O_2N$ and NO_3^- as a source of nitrogen (not NH_4^+). Also use HCO_3^- as an only form of an oxidized carbon species. (20 points)

Solution)



- 4) Write the overall cell synthesis reaction, R_s , in an electron-equivalent form. Use the R_d derived from 1) and the R_c derived from 3). How much grams of molasses are needed per g of NO_3 -N consumed for the cell synthesis reaction? (20 points)

Solution)



$$g \text{ molasses needed}/g \text{ NO}_3\text{-N consumed} = \frac{\frac{1}{48} \text{ mole} \times 342 \text{ g molasses/mole}}{\frac{1}{28} \text{ mole} \times 14 \text{ g NO}_3\text{-N/mole}} = 14.25$$

- 5) From the calculations you did for 2) and 4), which growth state do you think is more favorable for efficient use of molasses? (A) a rapidly growing state or (B) a slowly growing state? Briefly describe the reason for your selection. (10 points)

Solution)

(B)

At a slowly growing state, the f_e value is greater, meaning that the overall stoichiometry is more weighted to R_e than it is for a rapidly growing state. Therefore, at a slowly growing state the amount of molasses needed to remove a gram of $\text{NO}_3\text{-N}$ will be greater (more efficient use of molasses).

- 6) You are planning to control the molasses supply rate and other environmental conditions relevant to the bacterial growth such that a f_s value of 0.05 is achieved. Write the stoichiometry of the overall reaction occurring at this condition. For 1 g of $\text{NO}_3\text{-N}$ consumption, i) how much molasses will be consumed (in g molasses), ii) how much alkalinity will be produced (in g as CaCO_3), and iii) how much biomass will be produced (in g biomass)? (30 points)

Solution)

$$f_s = 0.05, f_e = 0.95$$

$$\begin{aligned} f_s R_s: & 0.001042 C_{12}H_{22}O_{11} + 0.001786 NO_3^- \\ & = 0.001786 C_5H_7O_2N + 0.003571 HCO_3^- + 0.001786 H^+ + 0.002530 H_2O \end{aligned}$$

$$f_e R_e: 0.01979 C_{12}H_{22}O_{11} + 0.19 NO_3^- = 0.095 N_2 + 0.2375 HCO_3^- + 0.0475 H^+ + 0.07521 H_2O$$

$$\begin{aligned} R: & 0.02083 C_{12}H_{22}O_{11} + 0.1918 NO_3^- \\ & = 0.001786 C_5H_7O_2N + 0.2411 HCO_3^- + 0.095 N_2 + 0.04929 H^+ + 0.07774 H_2O \end{aligned}$$

i) molasses consumption

$$\frac{0.02083 \text{ mole} \times 342 \text{ g molasses/mole}}{0.1918 \text{ mole} \times 14 \text{ g NO}_3\text{-N/mole}} = 2.65 \text{ g molasses/g NO}_3\text{-N}$$

ii) alkalinity production

HCO_3^- : alkalinity-contributing species; H^+ : alkalinity-consuming species

Total alkalinity produced = 0.2411 - 0.04929 = 0.1918 equivalent (for 1 e⁻ equivalent reaction)

Per g NO₃-N basis,

$$\frac{0.1918 \text{ eq} \times 50 \text{ g as CaCO}_3}{0.1918 \text{ mole} \times 14 \text{ g NO}_3 - \text{N/mole}} = 3.57 \text{ g as CaCO}_3 / \text{g NO}_3 - \text{N}$$

iii) biomass production

$$\frac{0.001786 \text{ mole} \times 113 \text{ g cells/mole}}{1918 \text{ moles} \times 14 \text{ g NO}_3 - \text{N/mole}} = 0.0752 \text{ g cells/g NO}_3 - \text{N}$$

2. At the following conditions, at what O₂ partial pressure will an energy reaction using ferric ion (Fe³⁺) as an e⁻ acceptor be more thermodynamically favorable than an energy reaction using O₂ as an e⁻ acceptor? From your results, briefly discuss about the condition where ferric ion reduction will be favorable.

$$pH=8.0$$

$$T=20^\circ C$$

$$[Fe^{2+}] = 8.0 \times 10^{-4} M \text{ (dissolved at the solubility limit of Fe(OH)}_2 \text{ at pH=8.0)}$$

$$[Fe^{3+}] = 4.0 \times 10^{-20} M \text{ (dissolved at the solubility limit of Fe(OH)}_3 \text{ at pH=8.0)}$$

(40 points)

Solution)

Ferrous-Ferric half-reaction:

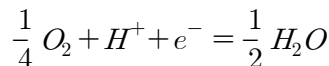


$$\Delta G_r^{\theta} = \Delta G_r^{\theta'} - RT \ln [10^{-7}] = \Delta G_r^{\theta'} = -74.27 \text{ kJ/e}^- \text{ eq}$$

$$\Delta G_r = \Delta G_r^{\theta} + RT \ln \frac{[Fe^{2+}]}{[Fe^{3+}]} = -74.27 + 8.314 \times 10^{-3} \text{ kJ/mole} - K \times 293 \text{ K} \times \ln \frac{8.0 \times 10^{-4}}{4.0 \times 10^{-20}}$$

$$= 17.16 \text{ kJ/e}^- \text{ eq}$$

Water-Oxygen half-reaction:



$$\Delta G_r^{\theta} = \Delta G_r^{\theta'} - RT \ln [10^{-7}] = -78.72 - 8.314 \times 10^{-3} \text{ kJ/mole} - K \times 298 \text{ K} \times (-1) \times \ln [10^{-7}]$$

(ΔG_r^θ is at 25°C)

$$= -118.65 \text{ kJ/e}^- \text{ eq}$$

$$\Delta G_r = \Delta G_r^{\theta} + RT \ln \frac{1}{P_{O_2}^{1/4} \cdot [H^+]} = -118.65 + 8.314 \times 10^{-3} \text{ kJ/mole} - K \times 293 \text{ K} \times \ln \frac{1}{P_{O_2}^{1/4} \cdot 10^{-8.0}}$$

$$= 17.16 \text{ kJ/e}^- \text{ eq}$$

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{1}{P_{O_2}^{1/4} \cdot [H^+]} = -118.65 + 44.87 + 8.314 \times 10^{-3} \text{ kJ/mole-K} \times 293 \text{ K} \times \frac{1}{4} \ln \frac{1}{P_{O_2}}$$

$$= 17.16 \text{ kJ/e}^- \text{ eq}$$

$$-\ln P_{O_2} = 149.33$$

$$\underline{P_{O_2} = 1.40 \times 10^{-65} \text{ atm}}$$

The results suggest that under any meaningful oxygen partial pressure, aerobic process will be more thermodynamically favorable than iron reduction.