Homework #2

Due: May 07 (Thu) 23:59

Question set I: Redox reactions

In this example question, we will compare the energy obtained by aerobic oxidation of glucose ($C_6H_{12}O_6$) and nitrification ($NH_4^+ \rightarrow NO_3^-$). In both processes, microorganisms use molecular oxygen (O_2) dissolved in water as an electron acceptor.

1) Pick up a pair of half reactions from Table 14.2 of the EOC textbook for each process. Combine the half reactions to write up the overall reaction for each process and calculate the $\Delta_r G^0(W)$ values. (10 points)

Answer)

It is convenient to convert the half reactions in an electron-equivalent form.

Aerobic glucose oxidation:

Use (1b) and convert:

$$\frac{1}{4}O_2(aq)+H^+ + e^- = \frac{1}{2}H_2O \qquad \Delta_r G^0(W) = -74.3\ kJ/e^-\ eq \qquad (a)$$

Use (12) and convert:

$$\frac{1}{4}CO_2(g)+H^+ + e^- = \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \qquad \Delta_r G^0(W) = 41.0\ kJ/e^-\ eq \qquad (b)$$

Overall reaction, (a) - (b):

$$\frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}O_2(aq) = \frac{1}{4}CO_2(g) + \frac{1}{4}H_2O$$

$$\Delta_r G^0(W) = -74.3 - 41.0 = -115.3\ kJ/e^-\ eq$$

Nitrification:

reduction half reaction is given above:

$$\frac{1}{4}O_2(aq)+H^+ + e^- = \frac{1}{2}H_2O \qquad \Delta_r G^0(W) = -74.3\ kJ/e^-\ eq \qquad (a)$$

Use (5) and convert:

$$\frac{1}{8}NO_3^- + \frac{5}{4}H + {}^{+}e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O \qquad \Delta_r G^0(W) = -35.0\ kJ/e^-\ eq \qquad (c)$$

Overall reaction, (a) - (c):

$$\frac{1}{8}NH_4^+ + \frac{1}{4}O_2(aq) = \frac{1}{8}NO_3^- + \frac{1}{4}H^+ + \frac{1}{8}H_2O$$

$$\Delta_r G^0(W) = -74.3 - (-35.0) = -39.3\ kJ/e^-\ eq$$

2) From the E_H^0 values of the half reactions, obtain the standard free energy change ($\Delta_r G^0$) of the half reactions. From the $\Delta_r G^0$ values for half reactions, calculate the standard free energy change of the two overall reactions. (15 points)

Answer)

Aerobic glucose oxidation:

i) oxygen reduction half reaction

$$\Delta_r G^0 = -nFE_H^0 = -1 \cdot 96.5\ kJ/mole - V \cdot 1.19\ V = -114.8\ kJ/e^-\ eq$$

ii) glucose oxidation half reaction

$$\Delta_r G^0 = -nFE_H^0 = -1 \cdot 96.5\ kJ/mole - V \cdot (-0.01\ V) = 1.0\ kJ/e^-\ eq$$

iii) overall reaction:

$$\Delta_r G^0 = -114.8 - 1.0 = -115.8\ kJ/e^-\ eq$$

Nitrification:

i) oxygen reduction half reaction: $\Delta_r G^0 = -114.8\ kJ/e^-\ eq$

ii) ammonium oxidation half reaction

$$\Delta_r G^0 = -nFE_H^0 = -1 \cdot 96.5\ kJ/mole - V \cdot 0.88\ V = -84.9\ kJ/e^-\ eq$$

iii) overall reaction:

$$\Delta_r G^0 = -114.8 - (-84.9) = -29.9\ kJ/e^-\ eq$$

3) Assume you added 90 mg/L glucose and 14 mg-N/L NH_4^+ into water at 25℃ and pH=7.0. You maintained the dissolved oxygen (DO) concentration in the water as 8 mg/L and inoculated a group microorganisms that mediate the two reactions. Calculate the $\Delta_r G$ values for both reactions. Assume the partial pressure of CO_2 as 3.0×10^{-4} atm and NO_3—N concentration of 0.1 mM. (15 points)

(Hint: assume molarity (M) equals activity for dissolved constituents. For gas constituents, use partial pressure as activity. Assume activity of water as 1.)

Answer)

Convert concentrations of all water constituents in molarity (M).

Glucose MW = 180 g/mole

glucose: $\frac{90\ mg/L}{180\ g/mole} \times 10^{-3}\ g/mg = 5.0 \times 10^{-4}\ M$

NH_4^+: $\frac{14\ mg-N/L}{14\ g/mole} \times 10^{-3}\ g/mg = 1.0 \times 10^{-3}\ M$

O_2: $\frac{8\ mg/L}{32\ g/mole} \times 10^{-3}\ g/mg = 2.5 \times 10^{-4}\ M$

$\Delta G_r = \Delta_r G^0 + RT \ln Q_r$

glucose aerobic oxidation:

$$Q_r = \frac{\{CO_2\}^{1/4}}{\{C_6H_{12}O_6\}^{1/24}\{O_2\}^{1/4}} = \frac{P_{CO_2}^{1/4}}{[C_6H_{12}O_6]^{1/24}[O_2]^{1/4}} = \frac{(3.0\times10^{-4})^{1/4}}{(5.0\times10^{-4})^{1/24}(2.5\times10^{-4})^{1/4}}$$

$= 1.437$

$\Delta G_r = \Delta_r G^0 + RT \ln Q_r = -115.8\ kJ/mole + (8.314\times10^{-3}\ kJ/K-mole)\cdot 298\ K \cdot \ln 1.437$

$= -114.9\ kJ/e^-\ eq$

Nitrification:

$$Q_r = \frac{\{NO_3^-\}^{1/8}\{H^+\}^{1/4}}{\{NH_4^+\}^{1/8}\{O_2\}^{1/4}} = \frac{[NO_3^-]^{1/8}[H^+]^{1/4}}{[NH_4^+]^{1/8}[O_2]^{1/4}} = \frac{(10^{-4})^{1/8}(10^{-7.0})^{1/4}}{(1.0\times10^{-3})^{1/8}(2.5\times10^{-4})^{1/4}}$$

$= 0.1062$

$\Delta G_r = \Delta_r G^0 + RT \ln Q_r = -29.9\ kJ/mole + (8.314\times10^{-3}\ kJ/K-mole)\cdot 298\ K \cdot \ln 0.1062$

$= -35.5\ kJ/e^-\ eq$

4) In the condition given in 3), which process is more competitive, glucose oxidation or nitrification? Can you guess how the glucose and ammonium concentration will change over time? (10 points)

Answer)

As glucose oxidation gives more energy than nitrification, glucose oxidation is more competitive. Therefore, glucose concentration will decrease first while nitrification does not occur significantly at the beginning of incubation. Later, as glucose is consumed, nitrification will get more and more competitive, because glucose oxidizing microorganisms will suffer from limited availability of glucose. In the sense of thermodynamics, Q_r *for glucose oxidation reaction will go up as glucose concentration decreases,* *resulting in reduced ΔG_r. Therefore, ammonium concentration will decrease once glucose is consumed substantially.*

Question set II: Nucleophilic reactions

Following concentrations for anionic constituents are determined for a water sample with a pH value of 7.0 at 25℃.

Constituents	Ionic weight	Concentration (mg/L)
NO_3^-	62.0	27.2
SO_4^{2-}	96.1	76.5
Cl^-	35.5	204.7
OH^-	17.0	can be derived from pH

The $n_{Nu,\,CH_3Br}$ values for the anions are shown below:

Anionic nucleophiles	$n_{Nu,\,CH_3Br}$
NO_3^-	1.0
SO_4^{2-}	2.5
Cl^-	3.0
OH^-	4.2

1) Determine the $[Nu]_{50\%}$ values for the anionic nucleophiles assuming s=1. Considering the $[Nu]_{50\%}$ values and the nucleophile concentrations, list nucleophiles that are significant for reaction with CH_3Br in the water. If the reaction rate for a nucleophile is more than 5% of the hydrolysis rate, determine the nucleophile as significant. (20 points)

Answer)

Firstly, calculate the molar concentration of the nucleophiles:

Nucleophile	*Ionic weight*	*Concentration (mg/L)*	*Concentration (M)*
NO_3^-	*62.0*	27.2	4.39×10^{-4}
SO_4^{2-}	*96.1*	76.5	7.96×10^{-4}
Cl^-	*35.5*	204.7	5.77×10^{-3}
OH^-			10^{-7}

$$[Nu]_{50\%} = 55.3 \times 10^{-n}_{Nu,\,CH_3Br}$$

Nucleophile	$n_{Nu,\,CH_3Br}$	*[Nu]* $[Nu]_{50\%}$ *(M)*	*[Nu] (M)*	$[Nu]/[Nu]_{50\%}$
NO_3^-	*1.0*	*5.53*	4.39×10^{-4}	7.94×10^{-5}
SO_4^{2-}	*2.5*	*0.175*	7.96×10^{-4}	4.55×10^{-3}
Cl^-	*3.0*	*0.0553*	5.77×10^{-3}	*0.104*
OH^-	*4.2*	3.49×10^{-3}	10^{-7}	2.87×10^{-5}

Concentration of all anions are smaller than $[Nu]_{50\%}$*. Therefore, water is the most significant nucleophile.*

As $k_{Nu}[Nu]_{50\%} = k_{H_2O}[H_2O]$

and

$k_{obs,Nu} = k_{Nu}[Nu]$ *(*$k_{obs,Nu}$*: pseudo-first order rate constant for Nu; Nu concentrations are all way higher than* $[CH_3Br]$ *provided)*

$$\frac{k_{obs,Nu}}{k_{obs,H_2O}} = \frac{k_{Nu}[Nu]}{k_{Nu}[Nu]_{50\%}} = \frac{[Nu]}{[Nu]_{50\%}}$$

Therefore, H_2O *and those with* $[Nu]/[Nu]_{50\%} > 0.05$ *are significant nucleophiles.*

Significant: H_2O *and* Cl^-

Insignificant: NO_3^-, SO_4^{2-}, OH^-

2) If 10^{-5} M of CH_3Br is added to the water sample, what will be the concentration of the products of nucleophilic substitution (including hydrolysis) after all the reactions occur completely? Consider only significant nucleophiles. (30 points)

Answer)

This is "reactions in parallel" problem.

CH_3Cl *production by* Cl^- *nucleophilic attack and* CH_3OH *production by hydrolysis are significant reactions.*

Because for parallel reactions $A\xrightarrow{k_1}B$ *and* $A\xrightarrow{k_2}C$ *(*k_1*,* k_2 *=* 1^{st} *order rate constants)*

$$\frac{d[A]}{dt}=-(k_1+k_2)[A]$$

and

$$\frac{d[B]}{dt}=k_1[A],\ \frac{d[C]}{dt}=k_2[A]$$

The product [B] and [C] after termination of the reaction will have the concentration ratio of k_1/k_2*.*

So:

$$[CH_3OH]_f=[CH_3Br]_i\times\frac{k_{obs,H_2O}}{k_{obs,H_2O}+k_{obs,Cl^-}}=[CH_3Br]_i\times\frac{1}{1+[Nu]/[Nu]_{50\%}}$$

$$=10^{-5}\,M\times\frac{1}{1+0.104}=9.06\times10^{-6}\,M$$

and

$$[CH_3Cl]_f=[CH_3Br]_i\times\frac{k_{obs,Cl^-}}{k_{obs,H_2O}+k_{obs,Cl^-}}=[CH_3Br]_i\times\frac{[Nu]/[Nu]_{50\%}}{1+[Nu]/[Nu]_{50\%}}$$

$$=10^{-5}\,M\times\frac{0.104}{1+0.104}=9.4\times10^{-7}\,M$$