

PROBLEMS/SOLUTIONS

1. Given that the Henry's law constant, K_H , for oxygen in water at 25°C is $1.3 \times 10^{-8} \text{ mol L}^{-1} \text{ Pa}^{-1}$, explain why a biological oxygen demand (BOD) value of $> 5 \text{ mg L}^{-1}$ is indicative of contaminated water.

Solution

$$K_H = 1.3 \times 10^{-8} \text{ mol L}^{-1} \text{ Pa}^{-1} \text{ (for O}_2 \text{ in water at 25°C)}$$

Show that $\text{BOD} > 5 \text{ mg L}^{-1}$ indicates contamination.

Consider a 1 L water sample and calculate the concentration of oxygen in equilibrium with the atmosphere (see Henry's Law, Chapter 11, Equation 11.2)

The partial pressure of O_2 is first determined by:

$$P_{\text{O}_2} = (P^\circ - P_{\text{H}_2\text{O}}) X_{\text{O}_2} \quad \begin{array}{l} P_{\text{H}_2\text{O}} \text{ at } 25^\circ\text{C} = 3.2 \times 10^3 \text{ Pa} \\ P^\circ = 101\,325 \\ X_{\text{O}_2} = 0.2095 \end{array}$$

$$P_{\text{O}_2} = (101\,325 - 3200) \times 0.2095 = 2.06 \times 10^4 \text{ Pa}$$

Now using Henry's law, the concentration of oxygen in the water at 25°C can be determined.

$$\begin{aligned} [\text{O}_2] &= K_H P_{\text{O}_2} = 1.3 \times 10^{-8} \text{ mol L}^{-1} \text{ Pa}^{-1} \times 2.06 \times 10^4 \text{ Pa} \\ &= 2.67 \times 10^{-4} \text{ mol L}^{-1} \quad (\times 32.0 \text{ g mol}^{-1} \times 1000 \text{ mg g}^{-1}) \end{aligned}$$

$$\text{or} \quad = 8.6 \text{ mg L}^{-1} \text{ (ppm)}$$

Therefore in one litre of water there is a potential of having 8.6 ppm O_2 dissolved at 25°C.

The BOD value represents how much oxygen is consumed during the 5-day test period.

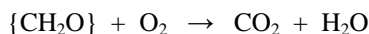
In this case a BOD of 5 mg L^{-1} (or greater) would result with the water having a final concentration of $3.6 \text{ mg L}^{-1} \text{ O}_2$ (or less). This concentration of O_2 is insufficient to support some forms of aquatic life and the water is said to be contaminated.

2. Consider dissolved organic matter to have the generic formula $\{\text{CH}_2\text{O}\}$. For a 1 mg L^{-1} (as C) aqueous solution of organic matter, calculate the mg of dissolved oxygen in the same volume required to oxidize it completely. Use this calculation to establish a relation between COD and DOC. Repeat the calculation using the generic formula for dissolved humic material (Fig. 12.3). Assume reaction of only the carbon and hydrogen in the humic material.

Solution

see Chapter 12, Figure 12.3

$$1 \text{ mg L}^{-1} \text{ (as C)} \text{ converts to } 8.33 \times 10^{-5} \text{ mol L}^{-1} \text{ (as C)}$$



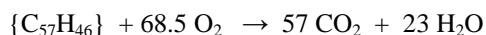
consider 1 L of solution:

We therefore have 8.33×10^{-5} mol of C or $\{\text{CH}_2\text{O}\}$ and therefore 8.33×10^{-5} mol of O_2 are also required. The mass of O_2 can now be determined.

$$8.33 \times 10^{-5} \text{ mol } (\text{O}_2) \times 32.0 \text{ g mol}^{-1} \times 1000 \text{ mg g}^{-1} = 2.7 \text{ mg of } \text{O}_2$$

Therefore each 1 ppm of C (or DOC) in 1 L of solution requires 2.7 mg of oxygen (COD)

Using a M.W. of 1056 g mol^{-1} and formula of $\text{C}_{57}\text{H}_{46}\text{O}_{18}\text{N}_2$, determined from Figure 12.3, but considering only the oxidation of C and H gives:



For 1 ppm as C

This again means having

$$8.33 \times 10^{-5} \text{ mol C or } 8.33 \times 10^{-5} / 57 = 1.46 \times 10^{-6} \text{ mol of } \{\text{C}_{57}\text{H}_{46}\} \text{ and}$$

$$8.33 \times 10^{-5} / 57 \times 68.5 = 1.00 \times 10^{-4} \text{ mol of } \text{O}_2$$

$$1.00 \times 10^{-4} \text{ mol of } \text{O}_2 \times 32 \text{ g mol}^{-1} \times 1000 \text{ mg g}^{-1} = 3.2 \text{ mg of } \text{O}_2$$

Therefore each 1 ppm C from humic material requires 3.2 mg of oxygen (COD).

The increased amount of oxygen is a result having a higher C:O molar ratio in the humic material formula vs. the generic formula CH_2O .

3. In the iron fertilization experiment to increase growth of phytoplankton in the oceans, what chemical species of iron would you expect to be present at equilibrium, if the iron was initially added as iron(III) chloride?

Solution

Given that the oceans have a pH of around 8.3 and a pE in the range of 8-12, it would be expected that the predominant form of iron initially introduced would be in the form of precipitated amorphous iron(III) hydroxide. As time goes on the iron species that would be in equilibrium would include, $\text{Fe}(\text{OH})_3$, iron-organic matter complexes, various other iron hydroxyoxides and an exceedingly small amount of $\text{Fe}^{3+}(\text{aq})$. A total average concentration of iron in the oceans is $1.7 \times 10^{-9} \text{ mol L}^{-1}$.

4. For an organic-rich soil, under controlled conditions in the laboratory at temperatures maintained in the mesophilic ranges, 20 to 30°C, the rate of carbon dioxide production commonly ranges from 5 to 50 mg CO_2 per kg soil per day. Using these data estimate the number of kg of carbon dioxide released from a 1 ha field under the same temperature conditions.

Chapter 15

Microbiological processes

Solution

CO₂ released from a 1 ha field? Range of emission rates 5-50 mg kg⁻¹ day⁻¹

Use an average value of 27.5 mg kg⁻¹ day⁻¹

Assume a depth of 0.20 m for the active soil which covers 100 m x 100 m (1 ha)

The volume of soil being considered is 2000 m³ (assume a bulk density of 1.2 g mL⁻¹)

1.2 kg L⁻¹ x 2000 m³ x 1000 L m⁻³ = 2.4 x 10⁶ kg (of soil)

27.5 mg kg⁻¹ day⁻¹ x 1 day x 2.4 x 10⁶ kg = 6.6 x 10⁷ mg CO₂ (or 66 kg CO₂)

66 kg of CO₂ is produced from the 1 ha field during one day. This value would, of course, depend on many factors including the nature and content of OM in the soil, moisture, texture etc., as well as on the ambient temperature.

5. 'Mineralization' refers to the process by which organic forms of an element are broken down and converted to inorganic species. In environmental situations this is most often a microbiological process. For nitrogen, indicate what forms of the element might be present in water or soil as reactants and products of the mineralization process.

Solution

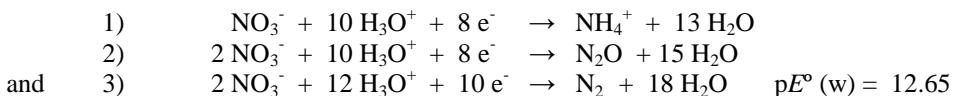
Reactants: (NH₂)₂CO (urea), uric acid, proteins (amino acids) H₂NCHRCOOH, humic material (HM), NTA nitrilotriacetic acid, herbicides (e.g. atrazine) and other pesticides (carbaryl)

Products: NH₃/NH₄⁺, NO₃⁻, NO₂⁻, N₂, N₂O

6. Use the thermochemical tables to calculate pE° values for the reductive half-reactions involving nitrate (NO₃⁻(aq)) in three different cases: when the product is; NH₄⁺(aq); N₂O (g); and N₂(g). Then calculate the pE°(w) values for the same three reactions. What is the environmental significance of these results?

Solution

Consider the reactions



$$pE^\circ = \frac{E^\circ}{0.0591} \quad (\text{Equation 10.44})$$

Use $\Delta G^\circ = -nFE^\circ$ to calculate E° (Equation 10.39)

Chapter 15**Microbiological processes**Calculate ΔG° by

$$\Delta G^\circ_{\text{rxn}} = \Sigma \Delta G^\circ_f(\text{products}) - \Sigma \Delta G^\circ_f(\text{reactants})$$

ΔG°_f values for:		kJ mol^{-1}
	NO_3^- (HNO ₃ aq)	- 111.3 (Appendix B.2)
	H_2O	- 237.2 (Appendix B.2)
	H_3O^+	- 237.2 (Appendix B.2)
	e^-	0 (Chapter 10)
	N_2	0 (Appendix B.2)
	N_2O	104.2 (Appendix B.2)
	NH_4^+	- 79.3 (Appendix B.2)
	NH_3 (aq)	- 26.6 (Appendix B.2)

For N_2 as a product: (Reaction 3 from above)

$$\Delta G^\circ_{\text{rxn}} = (0 + 18 \times -237.2) - (2 \times -111.3 + 12 \times -237.2 + 0)$$

$$= (-4269.6) - (-3069.0) = -1200.6 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ \quad -1.20 \times 10^6 \text{ J mol}^{-1} = -10 \times 96\,500 \text{ C mol}^{-1} \times E^\circ$$

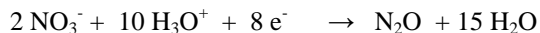
$$E^\circ = 1.244 \text{ V} \quad \& \quad pE^\circ = 1.244 \div 0.0591 = 21.1$$

$$\text{Using } pE = pE^\circ - 1/n \log \frac{P_{\text{N}_2}}{[\text{NO}_3^-]^2 [\text{H}_3\text{O}^+]^{12}} \quad \text{for calculation of } pE^\circ(w)$$

where $P_{\text{N}_2} = 1 \text{ atm}$, $[\text{NO}_3^-] = 1\text{M}$, $n = 10$ and $[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ M}$

$$pE = pE^\circ(w) \text{ at } \text{pH} = 7$$

$$pE^\circ(w) = 21.1 - 8.4 = 12.7 \text{ (approximately the same value as that found for Reaction 15.9)}$$

For N_2O as product: (Reaction 2 from above)

$$\Delta G^\circ_{\text{rxn}} = (104.2 + 15 \times -237.2) - (2 \times -111.3 + 10 \times -237.2 + 0)$$

$$= (-3453.8) - (-2594.6) = -859.2 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ \quad -8.59 \times 10^5 \text{ J mol}^{-1} = -8 \times 96\,500 \text{ C mol}^{-1} \times E^\circ$$

$$E^\circ = 1.113 \text{ V}$$

$$pE^\circ = 1.113 \div 0.0591 = 18.8$$

$$\text{Using } pE = pE^\circ - 1/n \log \frac{P_{\text{N}_2\text{O}}}{[\text{NO}_3^-]^2 [\text{H}_3\text{O}^+]^{10}} \quad \text{for calculation of } pE^\circ(w)$$

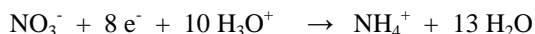
Chapter 15**Microbiological processes**

where $P_{\text{N}_2\text{O}} = 1 \text{ atm}$, $[\text{NO}_3^-] = 1 \text{ M}$, $n = 8$ and $[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ M}$

$$pE = pE^\circ(w) \text{ at } \text{pH} = 7$$

$$pE^\circ(w) = 18.8 - 8.75 = 10.1$$

For NH_4^+ as product: (Reaction 1 from above)



$$\Delta G^\circ_{\text{rxn}} = (-79.3 + 13 \times -237.2) - (-111.3 + 10 \times -237.2 + 0)$$

$$= (-3162.9) - (-2483.3) = -679.6 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ \quad -6.796 \times 10^5 \text{ J mol}^{-1} = -8 \times 96\,500 \text{ C mol}^{-1} \times E^\circ$$

$$E^\circ = 0.880 \text{ V}$$

$$pE^\circ = 0.880 \div 0.0591 = 14.9$$

$$\text{Using } pE = pE^\circ - \frac{1}{n} \log \frac{[\text{NH}_4^+]}{[\text{NO}_3^-][\text{H}_3\text{O}^+]^{10}} \quad \text{for calculation of } pE^\circ(w)$$

where $[\text{NH}_4^+] = 1 \text{ M}$, $[\text{NO}_3^-] = 1 \text{ M}$, $n = 8$ and $[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ M}$

$$pE = pE^\circ(w) \text{ at } \text{pH} = 7$$

$$pE^\circ(w) = 14.9 - 8.75 = 6.2$$

Summary of results:

	pE°	$pE^\circ(w)$
$\text{N}_2(\text{g})$	21.1	12.7
$\text{N}_2\text{O}(\text{g})$	18.8	10.1
$\text{NH}_4^+(\text{aq})$	14.9	6.2

It would appear from these values that reduction to N_2 is the favoured reaction, but in the natural environment the situation is more complicated than can be described simply by pE° values. For one thing, the nature of the microorganisms found in a particular situation is very important in determining what will be the final product of the reduction of nitrate.

7. Evolution of ammonia is one process that can result in the transfer of nitrogen from an aqueous system to the atmosphere. Discuss environmental conditions that would favour such a process. Would you expect ammonia evolution to be significant: (a) in an acid bog; (b) in the oceans?

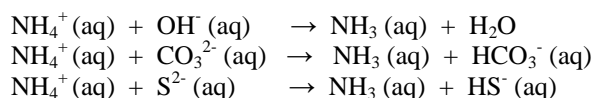
Solution

In the first instance, ammonia and/or ammonium ion are produced through ammonification reactions wherein organic forms of nitrogen are converted into these two species. Ammonia is also present in animal urine, and is an immediate product of the hydrolysis of urea, a common fertilizer.

Chapter 15**Microbiological Processes**

Environmental conditions that favour the evolution of ammonia from water include:

- the addition of base to the system (OH^- , CO_3^{2-} , S^{2-}) in the presence of NH_4^+ .
 $\text{pK}_a = 9.24$ (requires a very basic system)



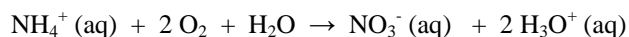
- mechanical mixing (aeration) to assist with the transfer of $\text{NH}_3(\text{aq})$ to $\text{NH}_3(\text{g})$.
- Note - $\text{NH}_3(\text{g})$ is very soluble in water ($K_H = 5.3 \text{ mol L}^{-1} \text{ atm}^{-1}$)

- Ammonia evolution would not likely be significant in an acid bog environment, since all of the ammonia would be in the (protonated) ammonium ion form.
 - Ammonia evolution from the oceans could be significant due to the higher pH where the potential for forming $\text{NH}_3(\text{aq})$ exists. The strong wave action and sea spray would assist in the ammonia exchange with the atmosphere.
8. For water with pH 6.7 and alkalinity of $110 \text{ mg CaCO}_3 \text{ L}^{-1}$, calculate the maximum concentration (mg N L^{-1}) of NH_4^+ that could be nitrified without the pH of the water falling below 6. Assume a closed system.

Solution

Given water with pH = 6.7, alkalinity of $110 \text{ mg CaCO}_3 \text{ L}^{-1}$ (100 g mol^{-1}) and the pH of water can fall to, but not below pH 6.

Nitrification of ammonia: (Reaction 15.1)



From this reaction we see that 1 mol of NH_4^+ produces 2 mol of H_3O^+ during the nitrification process.

How much acid can be consumed by the alkalinity? Consider a 1 L volume for this calculation.

$0.110 \text{ g} \div 100 \text{ g mol}^{-1} = 0.0011 \text{ mol}$ (of CaCO_3 or CO_3^{2-}) or the capacity to react with 0.0022 mol of H^+ .

Then $[\text{HCO}_3^-] = 0.0022 \text{ mol L}^{-1}$ (see Fig. 1.2) since virtually no CO_3^{2-} will exist at pH 6.7.

at pH 6.7:

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]} = 4.5 \times 10^{-7}$$

$[\text{H}^+] = 2.0 \times 10^{-7}$, $[\text{HCO}_3^-] = 0.0022$, and $[\text{CO}_2(\text{aq})] = 9.8 \times 10^{-4}$

The total amount of carbonate species is $0.0022 + 0.00098 = 3.18 \times 10^{-3} \text{ M}$

Chapter 15

Microbiological processes

Since the system is closed - there can be no change in the total amount of carbonate.

At pH 6 (the lowest the pH is allowed to fall) the total amount of carbonate is still 3.18×10^{-3} M

therefore

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2(aq)]} = 4.5 \times 10^{-7}$$

$$[HCO_3^-] + [CO_2] = 3.18 \times 10^{-3} \text{ or } [CO_2] = 3.18 \times 10^{-3} - [HCO_3^-]$$

$$K_{a1} = \frac{[10^{-6}][HCO_3^-]}{3.18 \times 10^{-3} - [HCO_3^-]} = 4.5 \times 10^{-7}$$

$$[HCO_3^-] = 9.8 \times 10^{-4}$$

$$\text{The change in } [HCO_3^-] = 2.2 \times 10^{-3} - 9.8 \times 10^{-4} = 0.00122 \text{ mol L}^{-1}$$

The amount of acid that can be consumed as the pH changes from 6.7 to 6.0 in the presence of 110 mg $CaCO_3$ is 1.22×10^{-3} mol of H^+ per 1 L.

That means that half of 1.22×10^{-3} (6.1×10^{-4} mol) of NH_4^+ (or mol of N) can be nitrified per 1 L.

Multiply the mol of N by 14.0 g mol^{-1} to give 8.5×10^{-3} g of N or ($\times 1000 \text{ mg g}^{-1}$) to give a concentration of 8.5 mg N L^{-1} that can be nitrified.

9. Why are reduced gaseous species of sulfur emitted from rice (paddy) fields, swamps, and the near shore borders of lakes, but not from open lakes—even though reduced sulfur compounds are found in the sediments in all these situations?

Solution

Reduced forms of sulfur compounds are released from rice fields, swamps and near shore borders of lakes as a result of the reducing conditions found within these environments. These are released directly into the atmosphere in their reduced forms, such as H_2S . In open lake water, despite the presence of reduced sulfur in the bottom sediments, there is an oxidizing environment in the overlying water into which these species are emitted. The higher pE conditions cause the oxidation of the reduced sulfur species to form soluble anions such as sulfate.

10. Would you expect gaseous sulfur emissions to be greater from the soil of a tropical savannah or of a tropical rainforest? What gaseous species are likely to be released?

Solution

It would be expected that the tropical rainforest would have greater gaseous sulfur emissions over that of the tropical savannah. The pE/pH, and temperature conditions that obtain in the rainforest (especially during the rainy season) likely create a variety of reduced sulfur species, due to the rapid growth and life cycles that involve microbiological activity (particularly those involving sulfur). The hot and drier tropical savannah on the other hand would be a more highly oxygenated environment. The smaller content of

Chapter 15**Microbiological Processes**

moisture in the soil would also limit (relatively) both the chemical and biological activity and therefore gaseous emissions from within.

The type of gaseous sulfur emissions expected from the tropical rainforest would be H₂S (g), CH₃SH (g), (CH₃)₂S (g), (CH₃)₂S₂ (g) and possibly CS₂ (g) and COS (g).

11. Using data from Appendix B.2, calculate the pE / pH equation for the SO_4^{2-} / SO_3^{2-} boundary. Plot it on the sulfur diagram. What is the significance of this plot in terms of the stability of the sulfite species in the hydrosphere.

Solution

(see Chapter 10, Figure 10.5, also reproduced below)

The first thing to realize is that the sulfite species that is of interest in the region between pH 1.8 and 7.2 is hydrogen sulfite HSO₃⁻. Sulfite (SO₃²⁻) itself is the predominant form above pH 7.2. A ΔG_f° value for these species is required for the calculation. We will consider only the redox process applying to the deprotonated form, but the conclusion is similar if one considers the amphoteric hydrogen sulfite.

Consider the reaction: $SO_4^{2-} (aq) + 2 e^- + 2 H_3O^+ (aq) \rightarrow SO_3^{2-} (aq) + 3 H_2O$

Thermodynamic Data:

		kJ mol^{-1}
ΔG_f° values for:	SO ₃ ²⁻	- 486.5
	HSO ₃ ⁻	- 527.8
	H ₂ O	- 237.2 (Appendix B.2)
	H ₃ O ⁺	- 237.2 (Appendix B.2)
	SO ₄ ²⁻	- 744.6 (Appendix B.2)
	e ⁻	0.0

$$\Delta G_{rxn}^\circ = [\Delta G_f^\circ(SO_3^{2-}) + 3 \times \Delta G_f^\circ(H_2O)] - [\Delta G_f^\circ(SO_4^{2-}) + 2 \times \Delta G_f^\circ(H_3O^+) + 2 \times \Delta G_f^\circ(e^-)]$$

$$\Delta G_{rxn}^\circ = (-486.5 + 3 \times -237.2) - (-744.6 + 2 \times -237.2 + 0)$$

$$= (-1198.1) - (-1219.0) = 20.9 \text{ kJ mol}^{-1}$$

From Equation 10.39 $\Delta G^\circ = -nFE^\circ$

$$20.9 \times 10^3 \text{ J mol}^{-1} = -2 \times 96\,500 \text{ C mol}^{-1} \times E^\circ$$

$$E^\circ = -0.108 \text{ V}$$

Use Equation 10.44 $pE^\circ = -0.108 \div 0.0591 = -1.83$

$$\text{Using } pE = pE^\circ - \frac{1}{n} \log \frac{[SO_3^{2-}]}{[SO_4^{2-}][H_3O^+]^2} \quad \text{for calculation of } pE(w)$$

where $[SO_3^{2-}] = 1 \text{ M}$, $[SO_4^{2-}] = 1 \text{ M}$, $n = 2$ and $[H_3O^+] = 1 \times 10^{-7} \text{ M}$
 $pE = pE(w) \text{ at } pH = 7 \quad pE(w) = -1.83 - 7 = -8.83$

Chapter 15**Microbiological processes**

For the line calculation:

Set the boundary condition at 10^{-2} M to be consistent with other calculations in Figure 10.5

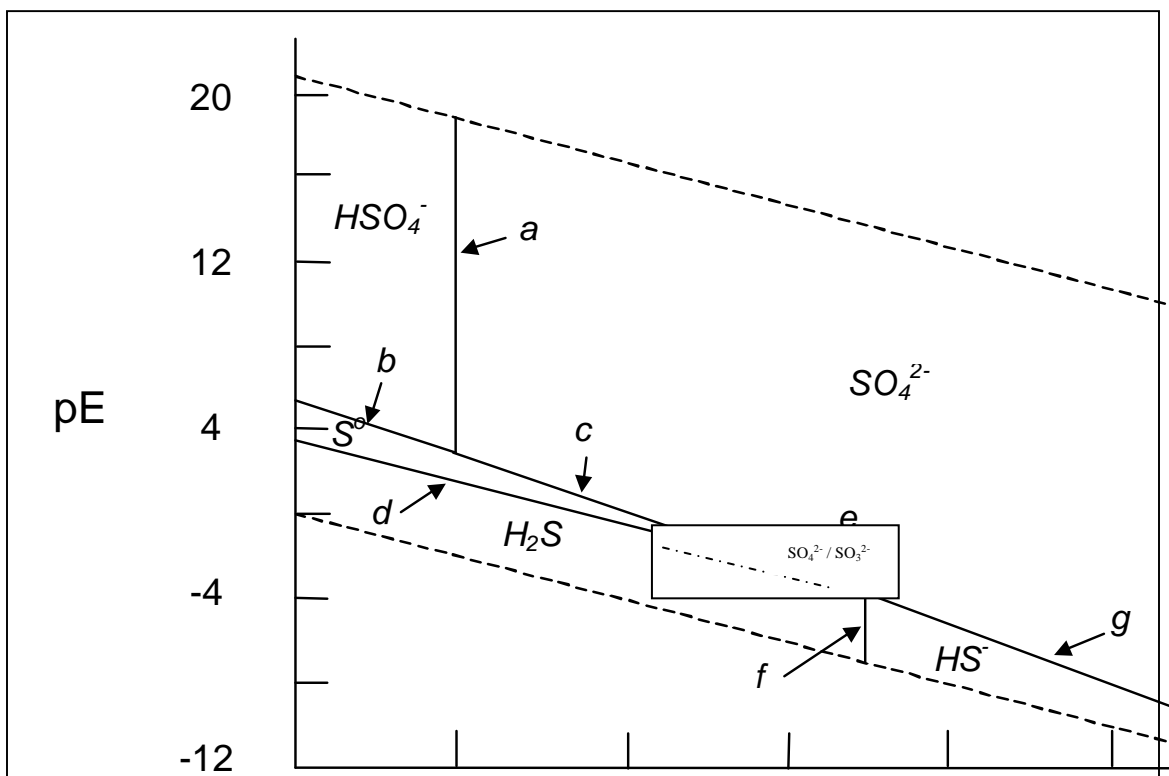
$$10^{-2} \text{ M} = [\text{SO}_4^{2-}] = [\text{SO}_3^{2-}], n = 2, \text{ pH} = -\log[\text{H}_3\text{O}^+]$$

$$pE^\circ = \frac{-\Delta G^\circ}{2.303nRT} = \frac{-20\,900}{2.303 \times 2 \times 8.315 \times 298} = -1.83$$

$$\text{Using } pE = pE^\circ - \frac{1}{n} \log \frac{[\text{SO}_3^{2-}]}{[\text{SO}_4^{2-}] [\text{H}_3\text{O}^+]^2}$$

Generates the line: $pE = -1.83 - \text{pH}$

When plotted on the pE / pH diagram for sulfur, the generated line (— · — · — · —) for the $\text{SO}_4^{2-} / \text{SO}_3^{2-}$ boundary, at pH values above 7.2, falls beneath that of the water stability line (-----). This would indicate that the sulfite species is not a thermodynamically stable form in water. However, the reactions involving their oxidation/decomposition are very slow, and therefore such species have been observed and are known to have a transient existence. Once again, this example shows that thermodynamic calculations do not tell the whole story about the behaviour of chemical species in water.



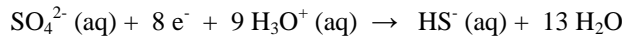
Chapter 15**Microbiological Processes**

12. The pE of a groundwater sample is -1.2 and the pH is 8.83 . The concentrations of SO_4^{2-} and HS^- are 2.29 and 0.003 mM, respectively. Is the system at equilibrium?

Solution

$$pE = -1.2 \quad pH = 8.83 \quad [SO_4^{2-}] = 2.29 \times 10^{-3} \text{ M} \quad [HS^-] = 3 \times 10^{-6} \text{ M}$$

Consider the equation:



Thermodynamic Data:

ΔG°_f values for:		kJ mol^{-1}
	$HS^- (aq)$	12.1 (Appendix B.2)
	H_2O	-237.2 (Appendix B.2)
	H_3O^+	-237.2 (Appendix B.2)
	$SO_4^{2-} (aq)$	-744.6 (Appendix B.2)
	e^-	0.0

$$\Delta G^\circ_{rxn} = [\Delta G^\circ_f(HS^-) + 13 \times \Delta G^\circ_f(H_2O)] - [\Delta G^\circ_f(SO_4^{2-}) + 8 \times \Delta G^\circ_f(e^-) + 9 \times \Delta G^\circ_f(H_3O^+)]$$

$$\Delta G^\circ_{rxn} = (12.1 + 13 \times -237.2) - (-744.6 + 0 + 9 \times -237.2)$$

$$= (-3071.5) - (-2879.4) = -192.1 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ \quad -1.921 \times 10^5 \text{ J mol}^{-1} = -8 \times 96\,500 \text{ C mol}^{-1} \times E^\circ$$

$$E^\circ = 0.249 \text{ V}$$

$$pE^\circ = 0.249 \div 0.0591 = 4.21$$

Using the given conditions - calculate pE :

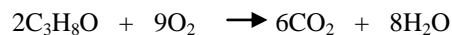
$$pH = 8.83, [H_3O^+] = 1.48 \times 10^{-9}, [SO_4^{2-}] = 2.29 \times 10^{-3} \text{ M}, [HS^-] = 3 \times 10^{-6} \text{ M}, n = 8$$

$$\text{Using } pE = pE^\circ - 1/n \log \frac{[HS^-]}{[SO_4^{2-}] [H_3O^+]^9}$$

$$pE = pE^\circ - 1/n \log \frac{[HS^-]}{[SO_4^{2-}] [H_3O^+]^9} = 4.21 - 9.573 = -5.36$$

Since -5.36 does not equal -1.2 the system is not at equilibrium.

13. Some n-propanol (0.2 t) is accidentally discharged into an approximately circular waste lagoon with radius 50 m and average depth of 2 m. What is the increase in BOD and in COD in the water? Assume complete degradation to CO_2 :



Chapter 15

Microbiological processes

Solution

$$\begin{aligned}
 0.2 \text{ t n-propanol (60.1 g mol}^{-1}\text{)} &= 200 \text{ kg n-propanol} \\
 &= 2 \times 10^5 \text{ g} \\
 \div 60.1 \text{ g mol}^{-1} &= 3328 \text{ mol n-propanol}
 \end{aligned}$$

From the above equation:

$$\begin{aligned}
 3328 \text{ mole n-propanol} \times 9/2 &= 14975 \text{ mol O}_2 \\
 \times 32.0 \text{ g mol}^{-1} &= 4.80 \times 10^5 \text{ g O}_2 \\
 &= 4.80 \times 10^8 \text{ mg O}_2
 \end{aligned}$$

Volume of water body:

$$\begin{aligned}
 \pi r^2 \times d &= 3.14 \times 2500 \text{ m}^2 \times 2 \text{ m} = 15708 \text{ m}^3 \\
 &= 1.57 \times 10^7 \text{ L}
 \end{aligned}$$

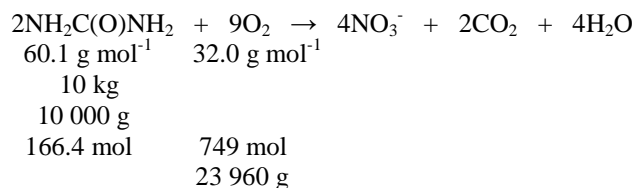
The increased demand on BOD (assuming complete degradation to CO₂) is:

$$4.80 \times 10^8 \text{ mg O}_2 \div 1.57 \times 10^7 \text{ L} = 30.6 \text{ mg L}^{-1} \text{ O}_2$$

Resistant compounds are oxidized under the harsh conditions of COD to a greater extent than in a BOD experiment, and therefore the COD is usually greater than BOD often by a factor of around two or more. However, in this example problem since the material is assumed completely degraded, the increase in COD would also be 30.6 mg L⁻¹ O₂.

- 14.** When excess fertilizer is carried from soil in runoff water, it increases the BOD of the water. Calculate the mass of oxygen required to oxidize 10 kg of urea. Assume that the nitrogen is oxidized to form nitrate.

Solution



24 kg of oxygen is required to oxidize 10 kg of urea.