

Thermodynamics

Solutions

Identifying Unknowns

1. What would be the equilibrium pH if gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dissolved in water?

ANSWER: Ca^{2+} , SO_4^{2-} , H^+ , OH^- , H_2O

2. What would be the equilibrium pH if $\text{Al}_2(\text{SO}_4)_3$ were dissolved in water?

ANSWER: SO_4^{2-} , Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_{3(s)}$, $\text{Al}(\text{OH})_4^-$, H^+ , OH^- , H_2O

3. What would be the equilibrium concentration of Cu^{2+} in water at pH 7.5 if tenorite ($\text{CuO}_{(s)}$) were to dissolve?

ANSWER: Cu^{2+} , CuOH^+ , $\text{Cu}(\text{OH})_2^0$, $\text{Cu}(\text{OH})_3^-$, H^+ , OH^- , H_2O

Identify equations

4. What would be the equilibrium pH if gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dissolved in water?

ANSWER: Ca^{2+} , SO_4^{2-} , H^+ , OH^- , H_2O – 5 unknowns

1. $K_w = \{\text{H}^+\}\{\text{OH}^-\}/\{\text{H}_2\text{O}\}$
2. $C_{\text{T-Ca}} = X$
3. $C_{\text{T-S}} = Y$
4. $[\text{H}^+] + 2[\text{Ca}^{2+}] = 2[\text{SO}_4^{2-}] + [\text{OH}^-]$
5. $\{\text{H}_2\text{O}\} = 1$

5. What would be the equilibrium pH if $\text{Al}_2(\text{SO}_4)_3$ were dissolved in water?

ANSWER: SO_4^{2-} , Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_{3(s)}$, $\text{Al}(\text{OH})_4^-$, H^+ , OH^- , H_2O - 8 unknowns

1. $K_w = \{\text{H}^+\}\{\text{OH}^-\}/\{\text{H}_2\text{O}\}$
2. $K_1 =$
3. $K_2 =$
4. $K_3 =$
5. $K_4 =$
6. $C_{\text{T-S}} = X$
7. $C_{\text{T-Al}} = 2/3X = [\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}^{3+}] + [\text{Al}(\text{OH})_{3(s)}] + [\text{Al}(\text{OH})_4^-]$
8. $3[\text{Al}^{3+}] + 2[\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{Al}(\text{OH})_4^-] + [\text{OH}^-]$

6. What would be the equilibrium concentration of Cu^{2+} in water at pH 7.5 if tenorite ($\text{CuO}_{(s)}$) were to dissolve?

ANSWER: Cu^{2+} , CuOH^+ , $\text{Cu}(\text{OH})_2^0$, $\text{Cu}(\text{OH})_3^-$, H^+ , OH^- , H_2O (6 unknowns)

1. $K_w = \{\text{H}^+\}\{\text{OH}^-\}/\{\text{H}_2\text{O}\}$
2. $K_1 =$
3. $K_2 =$
4. $K_3 =$
5. $C_{\text{T-Cu}} = [\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu}(\text{OH})_2^0] + [\text{Cu}(\text{OH})_3^-]$
6. $[\text{H}^+] + 2[\text{Cu}^{2+}] + [\text{CuOH}^+] = [\text{OH}^-] + [\text{Cu}(\text{OH})_3^-]$

Analytical Solutions

Approximations

Graphical approach

7. What would be the equilibrium pH if 1 L of 10^{-4} M NH_4OH were mixed with 100 mL of 0.001 M HCl? $\text{p}K_a(\text{NH}_4^+) = 9.2$, $\text{p}K_a(\text{HCl}) = -3.0$

SOLUTION:

The pC-pH diagram is shown below. C_T for both NH_4^+ and Cl^- are about 10^{-4} . Because HCl dissociates essentially completely, the concentration of Cl^- is 10^{-4} M at all pH values. The equilibrium point may be found by writing the proton condition:

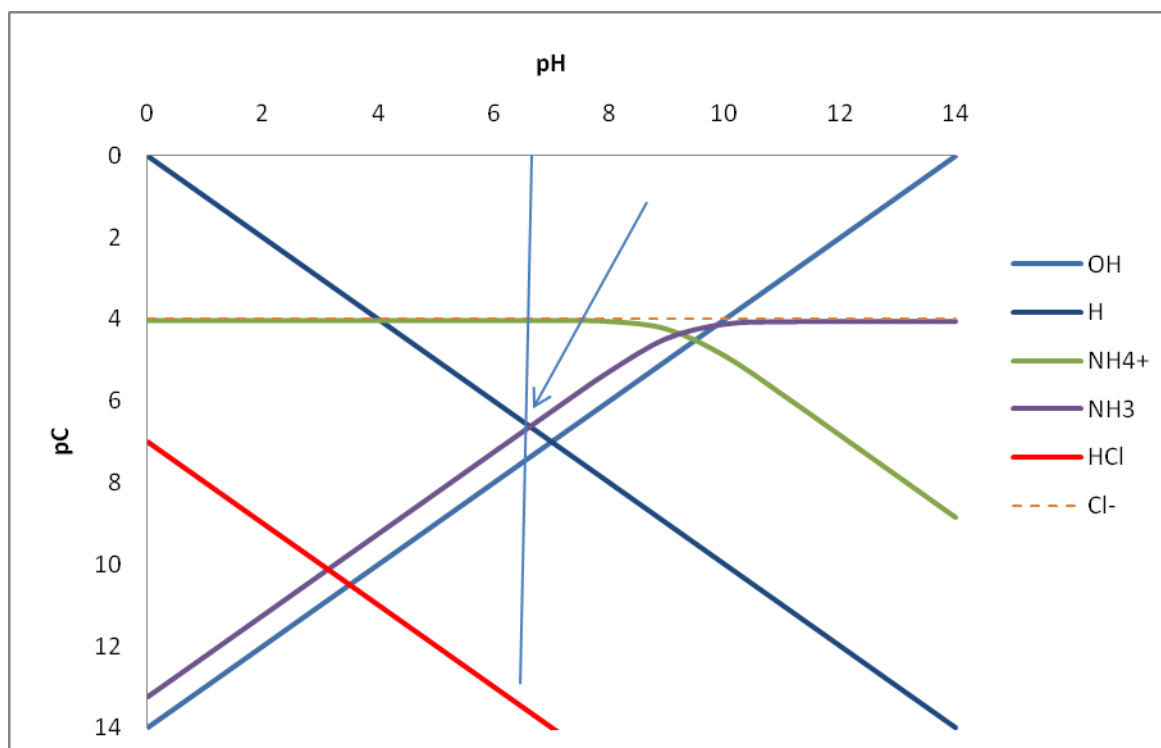
Species with more protons: HCl, H^+

Proton Reference Level: NH_4^+ , Cl^- , H_2O

Species with fewer protons: NH_3 , OH^-

Proton condition: $[\text{HCl}] + [\text{H}^+] = [\text{NH}_3] + [\text{OH}^-]$

To find this point, follow the H^+ line down to where it crosses NH_3 (see arrow). The pH is about 6.8. Since we have 10^{-4} M of both an acid and a base, we should expect that they will neutralize each other and the pH should be around 7.



8. What would be the equilibrium pH obtained by mixing 0.1 mole of sodium acetate with 1 L of 0.01 M HNO₃? pK_a(acetate) = 4.7, pK_a(HNO₃) = 0.

SOLUTION:

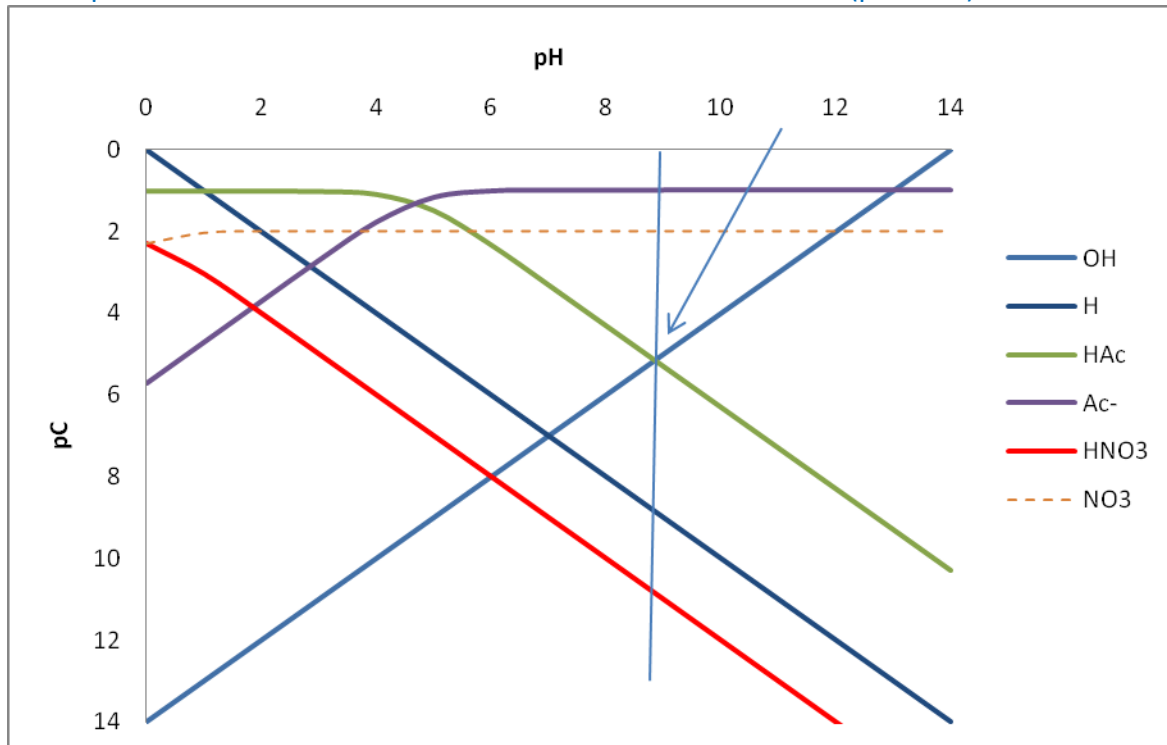
Here we are mixing a lot of a weak base with a little strong acid, so we should expect the pH to be lower than if the base alone were present, but still above 7.

To find the equilibrium pH, construct the proton condition:

Species with more protons: HAc, HNO₃, H⁺
 Proton Reference Level: Ac⁻, Na⁺, H⁺, NO₃⁻, H₂O
 Species with fewer protons: OH⁻

Proton Condition: [HAc] + [HNO₃] + [H⁺] = [OH⁻]

This equation is satisfied where the HAc line crosses the OH⁻ line (pH ~ 8.9)



9. What would be the pH of pure water in equilibrium with air with pCO₂ of 400 μatm?

SOLUTION:

Carbonic acid (H₂CO₃) is a polyprotic acid with pK_{a1} of 6.3 and pK_{a2} of 10.3. The system is open, and as a result, [H₂CO₃*] is constant at all pH values to be in equilibrium with CO₂(g).

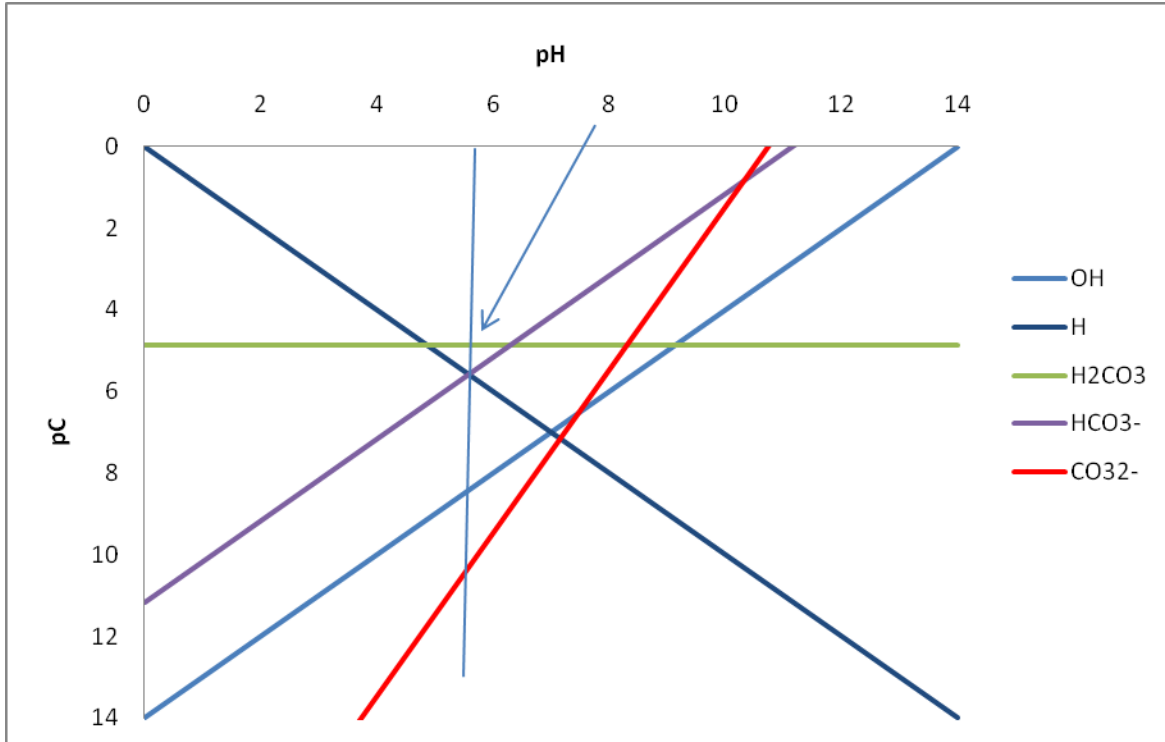
$$[H_2CO_3^*] = K_H \cdot pCO_2 = 10^{-1.46} \cdot 400 \times 10^{-6} = 10^{-4.86} M$$

The HCO₃⁻ line may be computed as a function of H₂CO₃*: [HCO₃⁻] = K_{a1}[H₂CO₃*]/[H⁺], and the CO₃²⁻ line may be calculated from this line as: [CO₃²⁻] = K_{a2}[HCO₃⁻]/[H⁺]

The equilibrium pH occurs at solution of the proton condition:

Species with more protons: H^+
 Proton Reference Level: H_2CO_3^* , H_2O
 Species with fewer protons: HCO_3^- , OH^-
 Species with 2 fewer protons: CO_3^{2-}

Proton Condition: $[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$
 This equation is satisfied where the H^+ line crosses the HCO_3^- line (pH ~ 5.7)



10. What would be the equilibrium pH of water exposed to a large volume of a gas mixture containing 10% CO_2 and 90% H_2S . For CO_2 $\text{pK}_{a1} = 6.3$ and $\text{pK}_{a2} = 10.3$; For H_2S $\text{pK}_{a1} = 7.0$

Open Systems

11. If the concentration of dissolved atrazine in Lake Michigan is 40 ng/L and the concentration of gaseous atrazine in the air above the lake is 3×10^{-15} atm, will atrazine move from the air into the lake or vice versa?
 $P^o = 3.9 \times 10^{-10}$ atm
 $K_H = 3.3 \times 10^5$ mole/L-atm
 Solubility = 1.3×10^{-4} mole/L
 m.w. = 216 g/mole

SOLUTION:

The reaction involved is air-water partitioning, for which the equilibrium constant is the Henry's Law Constant (K_H). To determine the direction of the reaction, one can calculate Q/K.



$$Q = \frac{[A_{(aq)}]}{[A_{(g)}]} = \left(40 \frac{ng}{L}\right) \left(10^{-9} \frac{g}{ng}\right) \left(\frac{mole}{216g}\right) \left(\frac{1}{3 \times 10^{-15} atm}\right)$$

$$Q = 6.2 \times 10^4 \frac{mole}{L \cdot atm}$$

$$\frac{Q}{K_H} = \frac{6.2 \times 10^4 \frac{mole}{L \cdot atm}}{3.3 \times 10^5 \frac{mole}{L \cdot atm}} = 0.19$$

Because Q/K is less than one, the reaction will proceed to the right with gaseous atrazine dissolving into the lake.

- b. What would be the concentration of atrazine in the lake that would be in equilibrium with the gaseous concentration given above ($3 \times 10^{-15} atm$)?

SOLUTION:

At equilibrium the dissolved concentration of atrazine would be:

$$K_H = \frac{[A_{aq}]}{[A_g]}$$

$$[A_{(aq)}] = K_H \cdot [A_{(g)}] = 3.3 \times 10^5 \frac{mole}{L \cdot atm} \cdot 3 \times 10^{-15} atm$$

$$[A_{(aq)}] = 9.9 \times 10^{-10} \frac{mole}{K} \cdot 216 \frac{g}{mole} \cdot 10^9 \frac{ng}{g} = 214 \frac{ng}{L}$$

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12. Air sparging is one method of removing volatile contaminants from polluted ground water. In this process, the air is pumped into the ground water, and it rises in bubbles through the zone of contaminated water. The pollutants partition from the water into the air and are removed from the soil. The pollutants can be removed from the air stream by passing it through activated carbon to which the organic compounds will sorb. **Which compound would be the easiest and which would be the most difficult to remove from ground water by air sparging.** Explain your answer.

Compound	Use	Sat. Vapor Pressure (atm)	K_H (mole/L-atm)	Log(K_{ow})
Trichloroethylene	Solvent	9.8×10^{-2}	9.3×10^{-2}	2.4
Decane	Jet fuel component	1.7×10^{-3}	1.5×10^{-4}	5.7
Parathion	Pesticide	6.0×10^{-9}	8.2×10^3	3.1
Dieldrin	Pesticide	3.3×10^{-9}	79	4.1
Trifluralin	pesticide	6.2×10^{-8}	14	3.9

ANSWER:

In order for the compound to be removed from the groundwater, it must not be sorbed strongly to the soil (it must have low K_{ow}) and it must partition readily from water into air (it must have low K_H). The compound that has the lowest K_H (decane) has the highest K_{ow} and hence it would not be readily removed by sparging. The compound with the next lowest K_H is TCE, and this compound has the lowest K_{ow} so it can both partition into air from the water and desorb readily from the soil. **Therefore, TCE would be the easiest compound to remove by air sparging.** The most difficult compound to remove will have a high K_H and high K_{ow} . Without doing the calculations in question 6 below, it is difficult to know whether Parathion or Dieldrin will be the most difficult to remove.

13. What concentration of oxygen would you expect to find in Lake Superior in summer when the water temperature is 18°C and the Henry's Law Constant for O_2 is 0.00141 mole/L-atm? **(9.45 mg/L)**

SOLUTION:

$$K_H = \frac{[O_2]_{(aq)}}{[O_2]_{(g)}}$$

$$[O_2]_{(aq)} = K_H \cdot [O_2]_{(g)}$$

$$[O_2]_{(aq)} = \left(0.00141 \frac{\text{mole}}{\text{L} \cdot \text{atm}}\right)(0.21 \text{atm}) = 2.96 \times 10^{-4} \frac{\text{mole}}{\text{L}}$$

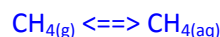
$$\left(2.96 \times 10^{-4} \frac{\text{mole}}{\text{L}}\right) \left(32 \frac{\text{g}}{\text{mole}}\right) \left(10^3 \frac{\text{mg}}{\text{g}}\right) = 9.45 \frac{\text{mg}}{\text{L}}$$

14. If the concentration of $CO_{2(g)}$ in the atmosphere is 3.7×10^{-4} atm, the concentration of $CO_{2(aq)}$ in the lake is 4.7 μM , and the Henry's Law Constant is $10^{-1.46}$ mole L^{-1} atm $^{-1}$, would the CO_2 partition into or out of the lake? Back up your conclusion with the appropriate calculations.

15. You are in charge of repairing the sewer mains for New York City. Before you send a work crew into the main, you measure the methane ($CH_{4(g)}$) concentration and find it to be dangerously high at 0.01 atm. You wish to determine whether the methane is coming from anaerobic decomposition of the sewage or from an unidentified gas leak. You measure the $CH_{4(aq)}$ in the sewage in the pipe and find it to be 1 μM . Could the elevated $CH_{4(g)}$ be coming from the sewage, or is it coming from another source? The Henry's Law constant for methane is $10^{-2.82}$ mole/L-atm at 25°C. (Assume the temperature in the sewer main is about 25°C.)

SOLUTION:

The easiest way to answer this question is to compute Q/K and thereby determine whether the methane is coming out of or going into the sewage. The value of K_H is given to us as $10^{-2.82}$ mole/L-atm. Now we must calculate Q.



$$Q = \frac{[CH_{4(aq)}]}{[CH_{4(g)}]} = \frac{\left(1 \frac{\mu\text{mol}}{L}\right) \left(10^{-6} \frac{\text{mole}}{\mu\text{mole}}\right)}{0.01 \text{atm}} = 10^{-4} \frac{\text{mole}}{L \cdot \text{atm}}$$

$$\frac{Q}{K} = \frac{10^{-4} \frac{\text{mole}}{L \cdot \text{atm}}}{10^{-2.82} \frac{\text{mole}}{L \cdot \text{atm}}} = 0.066$$

Because the value of Q/K is much less than one, the reaction has not yet reached equilibrium and would continue to go to the right. In other words, the gaseous methane would dissolve into the sewage, and could not be degassing from the sewage. There must be another source of methane besides the anaerobic sewage decomposition.

16. For workers in metal plating industries, the greatest danger from cyanide is from breathing HCN. The protonated form, HCN, is volatile. If the total concentration of cyanide (i.e., HCN + CN⁻) was 10 M, what fraction of the total would exist as the volatile form at a pH of 12? (**0.2%**)

ANSWER:

The fraction that exists as HCN equals: $[HCN]/([HCN] + [CN^-]) = [HCN]/10 \text{ M}$

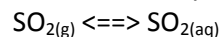
Therefore, we must solve for the concentration of [HCN] that would exist at pH 12.

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = \frac{[H^+](10M - [HCN])}{[HCN]}$$

$$[HCN] = \frac{(10M) \cdot [H^+]}{K_a + [H^+]} = \frac{(10M)(10^{-12} M)}{(10^{-9.3} + 10^{-12})} = 0.02M$$

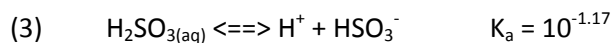
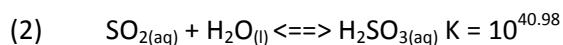
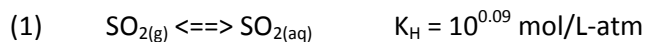
$$\frac{0.02M}{10M} = 0.002 = 0.2\%$$

17. In flue gas desulfurization (scrubbing), the SO_{2(g)} that is produced by combustion of sulfur in the fossil fuel is removed by allowing it to partition into water.



a) What are the name and one set of possible units of the equilibrium constant that governs this reaction?

b) The SO_{2(aq)} reacts with water to form H₂SO_{3(aq)} which is an acid. Thus, the following sequence of reactions is possible.



Would removal of SO_{2(g)} from the flue gases into the water be most effective at high or low pH? Explain your answer with the aid of a pC-pH diagram.

18. A pond on an industrial site is found to be saturated with trichloroethylene. The engineering firm remediating the site pumps one million liters of the pond water into a holding tank with a volume of 2 million liters; the opening of the tank is sealed. Two weeks later, the liquid is pumped to a bioreactor where the trichloroethylene is to be biodegraded. What would you expect the concentration of the trichloroethylene to be when the water reaches the bioreactor? Assume the temperature is constant at 25°C. (20 pts)

Trichloroethylene = C_2HCl_3

Solubility of trichloroethylene = 1100 mg/L

$K_H = 114 \text{ mole m}^{-3} \text{ atm}^{-1}$

(To receive partial credit, first explain why the concentration in the water will change.)

SOLUTION:

Some of the trichloroethylene (TCE) will partition from the water in the tank into the air in the headspace. Therefore, the concentration of TCE will be lower than the original concentration when it reaches the bioreactor.

The total mass of TCE present = $(1100 \text{ mg/L})(10^6 \text{ L}) = 1.1 \times 10^9 \text{ mg} = M_{\text{total}}$

The total mass of TCE must equal the mass in the water and that in the headspace:

$M_{\text{total}} = M_{\text{water}} + M_{\text{air}}$

$$M_{\text{water}} = \left(C_w \frac{\text{mole}}{\text{L}} \right) (10^6 \text{ L}) \left(\text{Mol.wt.} \frac{\text{g}}{\text{mole}} \right) \left(10^3 \frac{\text{mg}}{\text{g}} \right) = 10^9 \cdot C_w \cdot \text{Mol.wt.}$$

$$M_{\text{air}} (\text{mg}) = \left(C_{\text{air}} \frac{\text{mole}}{\text{L}} \right) (10^6 \text{ L}) \left(\text{Mol.wt.} \frac{\text{g}}{\text{mole}} \right) \left(10^3 \frac{\text{mg}}{\text{g}} \right) = 10^9 \cdot C_{\text{air}} \cdot \text{Mol.wt.}$$

The concentrations of TCE in the water and in the air are related through the Henry's Law constant.

$$K_H = \frac{[TCE]_{\text{water}}}{[TCE]_{\text{air}}} = \frac{\left(C_w \frac{\text{mole}}{\text{L}} \right)}{P_{\text{TCE}} (\text{atm})} = 0.114 \frac{\text{mole}}{\text{L} \cdot \text{atm}}$$

$$P_{\text{TCE}} (\text{atm}) = \frac{C_w}{K_H}$$

$$C_{\text{air}} \left(\frac{\text{mole}}{\text{L}} \right) = (P_{\text{TCE}} \text{ atm}) \left(\frac{1}{RT} \right)$$

$$C_{\text{air}} = \frac{C_w}{K_H \cdot RT}$$

Now, the expression for C_{air} and C_w can be substituted into the expression for M_{total} .

$M_{\text{total}} = M_{\text{water}} + M_{\text{air}}$

$$M_{\text{total}} = 10^9 \cdot \text{Mol.Wt.} \cdot C_w + 10^9 \cdot \text{Mol.Wt.} \cdot C_{\text{air}}$$

$$M_{\text{total}} = 10^9 \cdot \text{Mol.Wt.} \cdot C_w + 10^9 \cdot \text{Mol.Wt.} \cdot \frac{C_w}{K_H \cdot RT}$$

Solving for C_w yields:

$$C_w = \frac{M_{total}}{10^9 \cdot Mol.Wt.} \left(1 + \frac{1}{K_H \cdot RT} \right)^{-1}$$

The molecular weight of TCE = 2(12) + 1 + 3(35.5) = 131.5 g/mole
 Substituting values in the equation for C_w we obtain:

$$C_w = \frac{1.1 \times 10^9 \text{ mg}}{10^9 \cdot 131.5} \left(1 + \frac{1}{0.114 \cdot 0.082 \cdot 298} \right)^{-1} = 0.0062 \frac{\text{mole}}{\text{L}}$$

$$0.0062 \frac{\text{mole}}{\text{L}} \left(131.5 \frac{\text{g}}{\text{mole}} \right) \left(10^3 \frac{\text{mg}}{\text{g}} \right) = 809 \frac{\text{mg}}{\text{L}}$$

Of the initial 1100 mg/L, almost one third volatilized into the headspace.
