

Q1.

a) Name and discuss the mechanisms thought to occur during coagulation (5 points)

Solution:

- 1) Compression of electrical double layer and
- 2) Charge neutralization

**\*\*See book for more explanation**

b) If there is no bicarbonate present in a well water that is to be softened to remove magnesium, which chemical must you add? (2 points)

Solution:

If there is no bicarbonate, then the water has only noncarbonate hardness and the chemicals required are lime and sodium carbonate (soda ash).

c) Water softening is a chemical process aimed at reducing the presence of certain ions naturally present in the water. What are those ions, and, for each, under which new chemical form are they extracted from the water at the end of the treatment? (4 points)

Solution:

Calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ). Calcium carbonate ( $\text{CaCO}_3$ ) and magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ )

d) In a few words, explain physically why the depth  $H$  of a settling tank does not enter the expression for the critical settling velocity,  $V_c = Q/WL$ . (4 points)

Solution:

The particle removal efficiency increases with decreasing the depth/height of the sedimentation tank and a zero height will provide the maximum particle removal (theoretically). However, in practice it's not possible since a 2-dimensional structure won't be able to hold any water.

e) A can of a volatile chemical (benzene) has spilled into a small pond. List the data you would need to gather to calculate concentration of benzene in the stream leaving the pond using the mass balance technique. Assume steady state condition and no sorption of benzene to the bottom of the pond. (5 points)

Solution:

The approach to answer this question is to write a mass-balance equation for the system and use it to identify the data required for solution. In simplified terms, assume steady state and no sorption to the bottom of the pond.

Mass in = Mass that volatilizes + Mass that flows out of the pond downstream

The „Mass in“ is a function of the benzene concentration and the volume in the can.

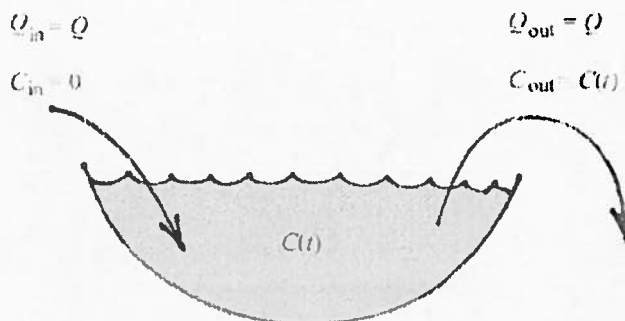
The „Mass that volatilizes“ can be estimated from Henry’s law and the rate of vaporization.

The mass that flows downstream may be estimated from the concentration and the flow rate of the stream. Because the concentration is the required unknown, the problem may be solved for concentration.

2. A bankrupt chemical company has been taken over by new management. On the property they found a 20,000 m<sup>3</sup> brine pond containing 25 g/L of salt and they propose to flush it through a discharge pipe leading to the Atlantic ocean, which is nearby and which has a salinity of 30 g/L. What flow rate of freshwater (in L/s) must they use to reduce the salinity of the pond to 500 mg/L within one year? (5 points)

$$C_t = C_0 e^{\left(-\frac{Q}{V}t\right)}; \quad 1 \text{ m}^3 = 1000 \text{ L}$$

Denote the salinity in the pond by its time-dependent concentration  $C(t)$ . Then make a mass budget with the control volume taken as the entire pond.



The salt budget takes the form:

$$V \frac{dC}{dt} = Q_{in} C_{in} - Q_{out} C_{out} + S - KVC$$

in which the source  $S = 0$  because there is no chemical formation of new salt inside the pond and  $K = 0$  because there is no reaction that removes salt from inside the pond. We also have:  $Q_{in} = Q_{out} = Q$ , the volumetric flow rate of the flushing.  $C_{in} = 0$  because the entering water is fresh (no salt content) and  $C_{out} = C(t)$  since the water being flushed out has the salinity of the water in the pond.

The budget then reduces to:

$$V \frac{dC}{dt} = -Q C(t)$$

The solution of this 1<sup>st</sup>-order differential equation is:

$$C(t) = C(t=0) \exp\left(-\frac{Q}{V}t\right)$$

Now, plug the numbers

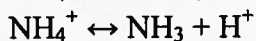
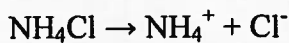
$$(500 \text{ mg/L}) = (25,000 \text{ mg/L}) \exp\left(-\frac{Q}{20,000 \text{ m}^3} \times 365 \text{ days}\right)$$

and solve for the flow rate  $Q$ . The solution is:

$$Q = 214.4 \frac{\text{m}^3}{\text{day}} = \frac{214.4 \times 10^3 \text{ L}}{\text{day}} = 2.48 \text{ L/s.}$$

3. One of the most common types of fertilizers used by farmers is a form of the highly soluble salt ammonium chloride ( $\text{NH}_4\text{Cl}$ ). At a certain farm, water runoff from fields carries dissolved ammonium chloride to a nearby pond, resulting in a dissolved concentration of  $\text{NH}_4\text{Cl}$  in the pond of 5 mg/L. At the same time, ammonia gas ( $\text{NH}_3$ ) is being produced by cows that feed around the farmer's pond, resulting in an atmospheric level of 500 ppb above the water surface.

In water, the following reactions take place



The first equation represents complete dissociation (dissolution of a salt), and the second equation is reversible with equilibrium constant  $[\text{NH}_3][\text{H}^+] / [\text{NH}_4^+] = 5.89 \times 10^{-10} \text{ M}$ . Assume that the ambient temperature is 25<sup>o</sup> C and the air pressure is 1 atm. Neglect the effects of other impurities such as  $\text{CO}_2$ . Calculate the pH of the pond water. (10 points)

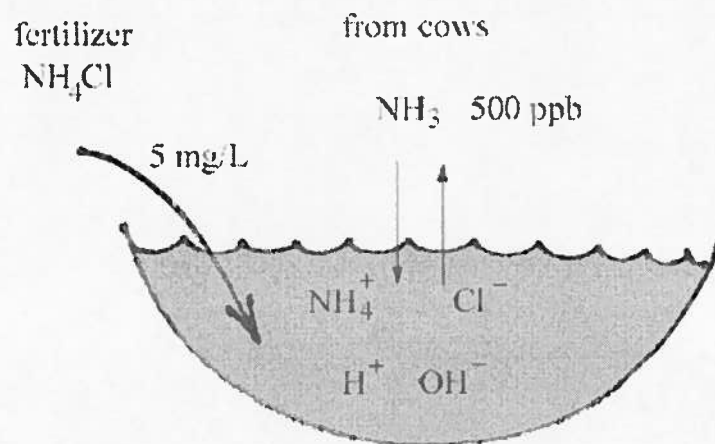
MW of  $\text{NH}_4\text{Cl}$ =53.5 g/mol;  $K_H$  (Henry's constant) = 62 M/atm;  $[\text{H}^+][\text{OH}^-] = 10^{-14}$

Molecular weights: H=1, N=14, Cl=35.5, O=16

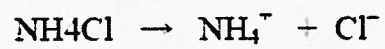
$\text{pH} = -\log_{10}[\text{H}^+]$ ;  $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ ;  $[\text{NH}_3] = K_H P_{\text{NH}_3}$ ;  $P_{\text{HH}_3} = \text{mole fraction} \times P_{\text{total}}$ ;

$\text{ppb} = V_i/V_{\text{total}} \times 10^9 = \text{moles}_i/\text{moles}_{\text{total}} \times 10^9$

(a) The chemistry of the pond and surrounding air consists of the following elements:



The fertilizer is a salt, which dissociated completely in the water. Thus,



While the ammonium ion  $\text{NH}_4^+$  undergoes additional chemical changes, the  $\text{Cl}^-$  ion remains inactive. Its concentration is then entirely due to the  $\text{NH}_4\text{Cl}$  input.

To get that concentration, we first need to convert the given mass amount of  $\text{NH}_4\text{Cl}$  into moles. For this, we begin with the molecular weight of this molecule:

$$\text{MW of } \text{NH}_4\text{Cl} = 14 + 4 \times 1 + 35.50 = 53.50 \text{ g/mol}$$

The number of moles of  $\text{NH}_4\text{Cl}$  in a 5 mg/L solution is:

$$\frac{5 \times 10^{-3} \text{ g/L}}{53.50 \text{ g/mol}} = 9.35 \times 10^{-5} \text{ mol/L} = 9.35 \times 10^{-5} \text{ M}$$

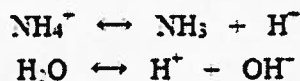
Since one molecule of  $\text{NH}_4\text{Cl}$  generates one ion of  $\text{Cl}^-$ , one mole of  $\text{NH}_4\text{Cl}$  generates one mole of  $\text{Cl}^-$ , and

$$[\text{Cl}^-] = 9.35 \times 10^{-5} \text{ M}$$

Another piece of information that we have is that the  $\text{NH}_3$  in the pond is in equilibrium with an atmospheric concentration of 550 ppb =  $550 \times 10^{-9}$  atm. By virtue of Henry's Law, with constant  $K_H$  read from table on page 96:

$$[\text{NH}_3] = K_H P_{\text{NH}_3} = (62 \text{ M atm})(550 \times 10^{-9} \text{ atm}) = 3.41 \times 10^{-5} \text{ M}$$

Now, we turn to the chemical reactions that occur in the water. There are two chemical equilibria



each with its constant of equilibrium:

$$\begin{aligned} \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} &= 5.89 \times 10^{-10} \text{ M} \Rightarrow \frac{[\text{H}^+]}{[\text{NH}_4^+]} = \frac{5.89 \times 10^{-10}}{3.41 \times 10^{-5}} = 1.73 \times 10^{-5} \\ [\text{H}^+][\text{OH}^-] &= 10^{-14} \text{ M}^2 \end{aligned}$$

To close the set of equations, we add the requirement of electroneutrality, which takes the form:

$$[\text{NH}_4^+] - [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

Since we already know  $[\text{NH}_3]$  and  $[\text{Cl}^-]$ , we have three equations for the following three unknowns:  $[\text{NH}_4^+]$ ,  $[\text{H}^+]$  and  $[\text{OH}^-]$ .

We are after the pH of the water, which demands that we know  $[H^+]$ . For this, we need to eliminate all other unknowns. Using the first two equations to solve for  $[NH_4^+]$  and  $[OH^-]$ , we substitute into the electroneutrality equation, to obtain:

$$\frac{[H^+]}{1.73 \times 10^{-2}} + [H^+] = 9.35 \times 10^{-2} + \frac{10^{-14}}{[H^+]}$$

of which the solution is  $[H^+] = 1.71 \times 10^{-9}$  M. [There is another solution, but it is negative and unphysical.] The pH is:

$$pH = -\log_{10}[H^+] = 8.77$$

This pH is above 7 (neutral water), and we conclude that the pond is alkaline.

4. A laboratory provides the following solids analysis for a wastewater sample: TS = 200 mg/L; TDS = 30 mg/L; FSS = 30 mg/L. (a) what is the total suspended solids concentration of this sample? ( 2 points) (b) Does this sample have appreciable organic matter? Why or why not? (3 points)

a)

$$TSS = TS - TDS = 200 \frac{mg}{L} - 30 \frac{mg}{L} = \boxed{170 \frac{mg}{L}}$$

b)

$$VSS = TSS - FSS = 170 \frac{mg}{L} - 30 \frac{mg}{L} = 140 \frac{mg}{L}$$

Because volatile solids consist primarily of organic matter, it can be concluded that approximately 70% (140/200) of the solids are organic.

5. Water defined by the following analysis to be softened by excess-lime treatment in a two-stage system.

Component	mg/L	Equivalent weight (EW)	mg/L	mg/L as $\text{CaCO}_3$
$\text{CO}_2$	8.8	22	0.4	20
$\text{Ca}^{2+}$	70	20	3.5	175
$\text{Mg}^{2+}$	9.7	12.2	0.80	40
$\text{Na}^+$	6.9	23	0.30	15
Alk	115	50	2.30	115
$\text{SO}_4^{2-}$	96	48	2.0	100
$\text{Cl}^-$	10.6	35.5	0.30	15

*Handwritten notes: 1, 2, 3, 4 = column 2 / column 3, column 4 x 5*

The practical limits of removal can be assumed to be 30 mg/L of  $\text{CaCO}_3$  and 10 mg/L of  $\text{Mg}(\text{OH})_2$ , expressed as  $\text{CaCO}_3$ .

- a) Determine total, carbonate and non-carbonate hardness, expressed in mg/L as  $\text{CaCO}_3$  (3 points)
- b) Calculate the quantity of softening chemicals required in pounds, expressed in mg/L as  $\text{CaCO}_3$  (7 points)

Molecular weights: Ca=40; C=12, O=16

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soln:

$$\begin{aligned} \text{Total hardness (TH)} &= \text{Ca}^{2+} + \text{Mg}^{2+} \\ &= 175 + 40 \\ &= \underline{215 \text{ mg/l as CaCO}_3} \end{aligned}$$

Carbonate hardness

Alk < TH ; Carbonate hardness = alk  
(CH)

⇒ CH = 115 mg/L as CaCO<sub>3</sub>

Non carbonate hardness: (NCH)

NCH = TH - CH = 215 - 115 = 100 mg/L as CaCO<sub>3</sub>

Lime required:

0	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
0.9	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
CO <sub>2</sub>	2.3 meq/l	1.2 meq/l	0.3
		3.5	4.3 4.6

- 1) To react with CO<sub>2</sub> = 20 mg/L
- 2) To remove carbonate hardness (caused by Ca<sup>2+</sup>) react with Ca(HCO<sub>3</sub>)<sub>2</sub> = 115 mg/L
- 3) To remove Mg non carbonate hardness (to react with MgSO<sub>4</sub>) = 90 mg/L
- 4) Excess lime to raise pH (30-70 mg/L) = 30 mg/L

Total lime = 205 mg/L as CaCO<sub>3</sub>

Soda Ash required:

Soda ash = non carbonate hardness = 100 mg as CaCO<sub>3</sub>