SOLUTIONS MANUAL

THEORY AND PRACTICE OF WATER AND WASTEWATER TREATMENT

RONALD L. DROSTE

Solutions Manual to Accompany

Theory and Practice of Water and Wastewater Treatment

Ronald L. Droste

University of Ottawa

John Wiley & Sons, Inc.

New York • Chichester • Brisbane • Toronto • Singapore

Copyright © 1997 by John Wiley & Sons, Inc.

This material may be reproduced for testing or instructional purposes by people using the text.

ISBN 0-471-15357-5

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Printed and bound by Malloy Lithographing, Inc.

CONTENTS

CHAPTER 1 1
CHAPTER 2 13
CHAPTER 3 21
CHAPTER 4 37
CHAPTER 5 45
CHAPTER 6 69
CHAPTER 7 77
CHAPTER 8 83
CHAPTER 9 85
CHAPTER 10 91
CHAPTER 11 127
CHAPTER 12 173
CHAPTER 13 187
CHAPTER 14 211
CHAPTER 15 233
CHAPTER 16 259
CHAPTER 17 273
CHAPTER 18 309
CHAPTER 19 327
CHAPTER 20 345
CHAPTER 21 363

1. The molecular weights of N, H_2S, and $NaHCO_3$ are 14, 34.1, and 84, respectively.

   1 mg/L = 1 ppm; 1 μg/L = 10^{-6}g/10^3 g = 1 ppb = 10^{-3} ppm

   (a) 4.2 mg N/L = 4.2 ppm = 4 200 ppb

   $$4.2\ \frac{\text{mg N}}{\text{L}} \times \frac{1\text{ M}}{14\ 000\text{ mg}} = 3.00 \times 10^{-4}\text{ M} = 3.00 \times 10^{-4}\text{ m}$$

   (b) 12 μg H_2S/L = 12 ppb = 12 × 10^{-3} ppm

   $$12\ \frac{\mu\text{g}}{\text{L}} \times \frac{1\text{ M}}{34.1\ \times 10^{6}\ \mu\text{g}} = 3.52 \times 10^{-7}\text{ M} = 3.52 \times 10^{-7}\text{ m}$$

   (c) 1.36×10^{-3} M = 1.36×10^{-3} m

   $$1.36 \times 10^{-3}\ \frac{\text{mole}}{\text{L}} \times \frac{84\ 000\text{ mg}}{\text{mole}} = 114\text{ mg/L} = 114\text{ ppm} = 114 \times 10^{3}\text{ ppb}$$

2.

Substance	MW	Concentration	moles in 1 L	mole fraction
H_2O	18.0	1 000 g/L	55.56	1.00
NaCl	58.5	75 mg/L	1.28×10^{-3}	2.30×10^{-5}
$C_6H_{12}O_6$	180.0	120 mg/L	6.67×10^{-4}	1.20×10^{-5}
O_2	32.0	8 mg/L	2.50×10^{-4}	4.50×10^{-6}
$Ca(HCO_3)_2$	162.0	150 mg/L	9.26×10^{-4}	1.67×10^{-5}
$MgSO_4$	120.4	45 mg/L	3.74×10^{-4}	6.73×10^{-6}
KNO_3	101.1	15 mg/L	1.48×10^{-4}	2.66×10^{-6}
		Total	55.56	1.00

The last column was calculated after the total moles in the system was calculated.

3.

Substance	[ ], mg/L	MW	Factor	[ ] as N, mg/L
NO_2^-	0.40	46	14/46 = 0.304	0.12
NO_3^-	1.90	62	14/62 = 0.226	0.43
NH_3	0.70	17	14/17 = 0.824	0.58
NH_4^+	8.90	18	14/18 = 0.778	6.92
			Total	8.05

4. $$[\text{CO}] = 2.0\text{ ppm}\left(\frac{1\text{ mg}}{10^{6}\text{ mg}}\Big/\text{ppm}\right)\left(\frac{1.292\ 9\text{ g air}}{\text{L}}\right)\left(\frac{10^{3}\text{ mg}}{1\text{ g}}\right)\left(\frac{10^{3}\text{ L}}{1\text{ m}^{3}}\right)\left(\frac{10^{3}\ \mu\text{g}}{\text{mg}}\right)$$

   $$= 2.59 \times 10^{3}\ \mu\text{g/m}^{3}$$

5. (a) NH_4^+ has a net charge of +1. Each H has an oxidation number of +1. ∴ N has an oxidation number of –3.

SO_4^{2-} has a net charge of –2. The 4 O's each have an oxidation number of –2. $\therefore$ S has an oxidation number of +6.

Fe has an oxidation number that will make the overall compound neutral.

Fe ox. no. = –[2(+1) + 2(–2)] = +2

(b) The oxidation numbers on each H are +1 for a total contribution of +4.

The oxidation numbers on each O are –2 for a total contribution of –4.

The C–C bond makes no contribution. The C on the right is bonded to two O's, one of which has an H bonded to it. The ox. no. of this carbon is –[1(1) + 2(–2)] = +3. To maintain a neutral compound the oxidation number on the other C must be –3 (which can also be determined by noting that it is bonded to three H atoms).

6. The compound is neutral. The average oxidation number on each C is

$$\text{ox. no.} = -\frac{12(1)+6(-2)}{6} = 0.$$

7. $NaClO_4$: Na - +1; O - –2; x = –[1 + (4)(–2)] = +7

$NaClO_3$: Na - +1; O - –2; x = –[1 + (3)(–2)] = +5

ClO_2: O - –2; x = –(2)(–2) = +4

NaOCl: Na - +1; O - –2; x = –(1 – 2) = +1

HOCl: H - +1; O - –2; x = –(1 – 2) = +1

NH_2Cl: Because Cl is more electronegative than N it must have an oxidation number of –1. H - +1;

for N, x = –[–1 + 2(1)] = +1

$NHCl_2$: Cl - –1; H - +1; for N, x = –[2(–1) + 1) = +1

NCl_3: Cl - –1; for N, x = –3(–1) = +3

HCl: H - +1; x = –(1) = –1

8. (a) $6H_2O + 6CO_2 \Leftrightarrow C_6H_{12}O_6 + 6O_2$

(b) $Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \Leftrightarrow 2Al(OH)_3 + 3CO_2 + 3CaSO_4$

9. Nitrate is produced from the oxidation of ammonia in aerobic (oxygen is utilized) biological wastewater treatment.

(a) Determine which of the following core reactions is feasible and balance it.

i. $NH_3 + O_2 \approx NO_3^-$

ii. $NH_3 + O_2 \approx NO_3^- + H_2O$

iii. $NH_3 + O_2 \approx NO_3^- + H_2O + H^+$

iv. $NH_3 + O_2 \approx NO_3^- + H_2O + OH^-$

v. $NH_3 + O_2 \approx NO_3^- + H_2$

Only reaction (iii) is feasible because the charge will balance on each side of the equation. O needs to be multiplied by 2 on the left-hand side, which will not affect the charge balance.

$NH_3 + 2O_2 \approx NO_3^- + H_2O + H^+$

(b) Oxidation reaction for ammonia

Ammonium adds an additional H to the LHS and an additional positive charge. An H^+ is required on the RHS.

$NH_4^+ + 2O_2 \approx NO_3^- + H_2O + 2H^+$

10. In an electron transfer reaction, the oxidation number of oxygen decreases from 0 to –2. The equivalent weight of oxygen is 16/2 = 8 g. For O_2, each oxygen atom decreases its oxidation number from 0 to –2.

$O_2 + 4e^- \rightarrow 2O^{2-}$

The equivalent weight is 32/4 = 8 g. Also reaction 28 in Table 1.3 can be checked to show that the equivalent weight of O_2 is 8 g.

11. Use reactions 25 and 27 from Table 1.3. Reverse reaction 25.

$$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O = \frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$$

$$\underline{\left(\frac{5}{8}\right)\left[\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O\right]}$$

$$\frac{1}{8}NH_4^+ = \frac{1}{16}N_2 + \frac{1}{2}H^+ + \frac{3}{8}e^-$$

Normalizing the half-reaction to the transfer of 1 e^-: $\frac{1}{3}NH_4^+ = \frac{1}{6}N_2 + \frac{4}{3}H^+ + e^-$

The gram molecular weight of ammonium is

MW = 14.0 + 4(1.0) = 18.0 g

Its equivalent weight in this reaction is 18 g/3 = 6.0 g.

12. Use reactions 26 and 27 (or reactions 24 and 25) in Table 1.3 to find a half-reaction for NO_2^- and NO_3^-.

$$\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}N_2 + \frac{2}{3}H_2O$$

$$\frac{10}{6}\left(\frac{1}{10}N_2 + \frac{3}{5}H_2O = \frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-\right)$$

$$\frac{1}{6}N_2 + H_2O = \frac{1}{3}NO_3^- + 2H^+ + \frac{5}{3}e^-$$

$$\underline{\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}N_2 + \frac{2}{3}H_2O}$$

$$\frac{1}{3}NO_2^- + \frac{1}{3}H_2O = \frac{1}{3}NO_3^- + \frac{2}{3}H^+ + \frac{2}{3}e^-$$

$$\frac{3}{2}\left(\frac{1}{3}NO_2^- + \frac{1}{3}H_2O = \frac{1}{3}NO_3^- + \frac{2}{3}H^+ + \frac{2}{3}e^-\right)$$

$$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O = \frac{1}{2}NO_3^- + H^+ + e^-$$

$$\underline{\frac{1}{2}OCl^- + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O}$$

$$\frac{1}{2}NO_2^- + \frac{1}{2}OCl^- = \frac{1}{2}NO_3^- + \frac{1}{2}Cl^-$$

13. (a) The half-reactions involved are

$$\tfrac{1}{8}SO_4^{2-} + \tfrac{5}{4}H^+ + e^- = \tfrac{1}{8}H_2S + \tfrac{1}{2}H_2O$$

$$\tfrac{1}{2}Cl_2 + e^- = Cl^-$$

Reversing the reaction for sulfide and adding it to the chlorine reaction, the overall reaction is

$$\tfrac{1}{8}H_2S + \tfrac{1}{2}H_2O + \tfrac{1}{2}Cl_2 = \tfrac{1}{8}SO_4^{2-} + \tfrac{5}{4}H^+ + Cl^-$$

There is a net production of 1 H^+ for each 1/8 mole of S^{2-} oxidized. Because H^+ is on the right hand side, a high concentration of H^+ will favor the reaction to the left. Therefore a high pH (low $[H^+]$) favors the reaction to the right.

The half-reaction for permanganate-manganese dioxide is

$$\tfrac{1}{3}MnO_4^- + \tfrac{4}{3}H^+ + e^- = \tfrac{1}{3}MnO_2 + \tfrac{2}{3}H_2O$$

The overall reaction is

$$\tfrac{1}{8}H_2S + \tfrac{1}{3}MnO_4^- + \tfrac{1}{12}H^+ = \tfrac{1}{8}SO_4^{2-} + \tfrac{1}{3}MnO_2 + \tfrac{1}{6}H_2O$$

In this case a low pH (high $[H^+]$) would favor the reaction.

14. Although ions may have the same charge, different sizes of ions will be less mobile which affects current carrying ability. Charge interaction effects occur in more highly concentrated solutions which also affects equivalent conductance.

15. From Eq. (1.11) $\mu = 1.6 \times 10^{-5}\,\kappa$

From Eq. (1.10) $\mu = 2.5 \times 10^{-5}$ (TDS)

Equating the two: $1.6 \times 10^{-5}\,\kappa = 2.5 \times 10^{-5}$ (TDS)

$$\kappa = \frac{2.5 \times 10^{-5}}{1.6 \times 10^{-5}}(\text{TDS}) = 1.56\ (\text{TDS})$$

where TDS is in mg/L
κ is in μmhos/cm

16. Eq. (1.26): $k = A\exp\left(-\frac{E_a}{RT}\right)$ Eq. (1.27): $k_{T_2} = k_{T_1}\theta^{(T_2 - T_1)}$

From Eq. (1.26),

$$\frac{k_{T_2}}{k_{T_1}} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \exp\left[\frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)\right] = \exp\left[\frac{E_a}{RT_1T_2}(T_2 - T_1)\right]$$

$$\therefore\ \theta = e^{-\frac{E_a}{RT_1T_2}}$$

17. p = 0.21 atm, T = 25°C = 25° + 273.2° = 298.2°K

pV = nRT

R = 0.082 L-atm/°-mole

$$\frac{n}{V} = \frac{p}{RT} = \frac{0.21\text{ atm}}{(0.082\text{ L - atm/°-mole})(298.2°)} = 8.59 \times 10^{-3}\text{ M}$$

$$= \left(8.59 \times 10^{-3}\ \frac{\text{mole}}{\text{L}}\right)\left(\frac{32\ \text{g}}{\text{mole}}\right)\left(\frac{1\ 000\ \text{mg}}{\text{g}}\right) = 275\ \text{mg/L}$$

18. Air contains 21% oxygen and 79% nitrogen by volume. $p_T = 1$ atm.

$pV = nRT$

$p_{O2} = 0.21(1\ \text{atm}) = 0.21\ \text{atm}$

$R = 0.082$ L-atm/°-mole

$$\text{for } O_2\text{: } \frac{n}{V} = \frac{p}{RT} = \frac{0.21\ \text{atm}}{(0.082\ \text{L - atm/°-mole})(298.2°)} = 8.59 \times 10^{-3}\ \text{M}$$

$$= \left(8.59 \times 10^{-3}\ \frac{\text{mole}}{\text{L}}\right)\left(\frac{32\ \text{g}}{\text{mole}}\right) = 0.275\ \text{g/L}$$

$p_{N2} = 0.79(1\ \text{atm}) = 0.79\ \text{atm}$

$$\text{for } N_2\text{: } \frac{n}{V} = \frac{p}{RT} = \frac{0.79\ \text{atm}}{(0.082\ \text{L - atm/°-mole})(298.2°)} = 0.032\ 3\ \text{M}$$

$$= \left(0.032\ 3\ \frac{\text{mole}}{\text{L}}\right)\left(\frac{28\ \text{g}}{\text{mole}}\right) = 0.904\ \text{g/L}$$

The density of air at 0°C is

$\rho = 0.904 + 0.275 = 1.18$ g/L

(Other substances in atmospheric air slightly change this value.)

19. From Henry's law:

$C_s = K_H p_{N2}$

From Table 1.4, at 0°C for N_2, $K_H = 29.1$ mg/L-atm

From Dalton's law:

$p_{N2} = 0.79 p_T = 0.79(1.0) = 0.79$ atm

$C_s = (29.1\ \text{mg/L-atm})(0.79\ \text{atm}) = 23.0\ \text{mg/L}$

From Table 1.4, at 25°C for N_2, $K_H = 18.0$ mg/L/atm

$C_s = (18.0\ \text{mg/L/atm})(0.79\ \text{atm}) = 14.2\ \text{mg/L}$

20. The depth is 100 m and atmospheric air contains oxygen at 0.21 atm.

$C_s = K_H p_{O2}$

The total pressure at a depth of 100 m is $p = p_0 + \rho g h$

p_0 = atmospheric pressure = $101.3\ \text{kN/m}^2 = 101.3 \times 10^3\ \text{kg/m-s}^2$

The density of water, $\rho = 997.0\ \text{kg/m}^3$ at 25°C

$g = 9.81\ \text{m/s}^2$

The total pressure at a depth of 100 m is

$p = 101.3 \times 10^3 + (997.0\ \text{kg/m}^3)(9.81\ \text{m/s}^2)(100\ \text{m}) = 101.3 \times 10^3 + 978.1 \times 10^3\ \text{kg/m-s}^2$

$$= 1\ 079.4 \times 10^3 \text{ kg/m-s}^2 = \left(1\ 079.4 \times 10^3 \frac{\text{kg}}{\text{m - s}^2}\right)\left(\frac{1 \text{ atm}}{101.3 \times 10^3 \frac{\text{kg}}{\text{m - s}^2}}\right) = 10.66 \text{ atm}$$

The composition of gas will not change as it is compressed. From Dalton's law, the partial pressure of oxygen is

$$p_{O2} = \frac{n_1}{n_2} p_T = 0.21(1\ 079.4 \times 10^3 \text{ kg/m-s}^2) = 226.7 \times 10^3 \text{ kg/m-s}^2$$

$$= 2.24 \text{ atm}$$

Using Henry's law: C_s = (39.3 mg/L-atm)(2.24 atm) = 88.0 mg/L

21. At 0°C, the Henry's law constants for CH_4 and Cl_2 are given in Table 1.4 as 3 968 and 1 460 mg/L-atm, respectively. The units on the Henry's law constants are

$$K_H = \frac{[G(aq)]}{[G(g)]} = \frac{\text{mg/L}}{\text{atm}}; \quad K'_H = \frac{[G(aq)]}{[G(g)]} = \frac{\text{mole/L of solution}}{\text{mole/L of air}}$$

$$\frac{K'_H}{K_H} = \frac{\frac{\text{mole/L}}{\text{mg/L}}}{\frac{\text{mole/L}}{\text{atm}}} = \frac{\text{mole/mg}}{\text{mole/L - atm}} \quad \text{or} \quad K'_H = K_H \frac{\text{mole/mg}}{\text{mole/L - atm}}$$

At a temperature of 0°C and pressure of 1 atm, 1 mole of gas occupies 22.4 L. In the denominator, the number is 1/22.4 = 0.044 6. For CH_4, there is 1 mole/16 000 mg = 6.25×10^{-5} mole/mg; for Cl_2 there is 1 mole/70 900 mg = 1.41×10^{-5} mole/mg.

For CH_4: $K'_H = (1\ 460)\dfrac{6.25 \times 10^{-5}}{0.0446} = 2.05$

For Cl_2: $K'_H = (3\ 968)\dfrac{1.41 \times 10^{-5}}{0.0446} = 1.25$

22. (a) $C_0 = 2.6 \times 10^{-4}$ M, $k = 0.063\ h^{-1}$, T = 10°C, t = 2 h

$$\frac{dC}{dt} = -kC \Rightarrow C = C_0 e^{-kt}$$

$C = (2.6 \times 10^{-4} \text{ M})e^{-(0.063)(2)} = 2.29 \times 10^{-4}$ M

$\theta = 1.06$, at 30°C

$$k_{T_2} = k_{T_1}\theta^{(T_2 - T_1)} \Rightarrow k_{30} = (0.063\ h^{-1})(1.062)^{(30-10)} = 0.21\ h^{-1}$$

$C = (2.6 \times 10^{-4} \text{ M})e^{-(0.21)(2)} = 1.71 \times 10^{-4}$ M

(b) $$\frac{dC}{dt} = -kC^2 \Rightarrow \int_{C_0}^{C} \frac{dC}{C^2} = -k\int_0^t dt$$

$$-\frac{1}{C}\Big|_{C_0}^{C} = -kt, \qquad \frac{1}{C_0} - \frac{1}{C} = -kt$$

$$\frac{1}{C} = \frac{1}{C_0} + kt, \quad C = \frac{C_0}{1 + C_0 kt}$$

$$C = \frac{2.6 \times 10^{-4}\ \text{moles/L}}{1 + \left(2.6 \times 10^{-4}\ \text{moles/L}\right)\left(106.8\ \text{L/moles/h}\right)\left(2\ \text{h}\right)} = 2.46 \times 10^{-4}\ \text{M}$$

$\theta = 1.062$, at 30°C

$k_{30} = (106.8\ h^{-1})(1.062)^{(30-10)} = 355.7\ h^{-1}$

$$C = \frac{2.6 \times 10^{-4}\ \text{moles/L}}{1 + \left(2.6 \times 10^{-4}\ \text{moles/L}\right)\left(355.7\ \text{L/moles/h}\right)\left(2\ \text{h}\right)} = 2.19 \times 10^{-4}\ \text{M}$$

23. $\Delta T = 10°C = T_2 - T_1$; $\left(\frac{dC}{dt}\right)_{T_2} = 2\left(\frac{dC}{dt}\right)_{T_1}$

$$k_{T_2} C^n = 2 k_{T_1} C^n$$

$$k_{T_2} = k_{T_1} \theta^{(T_2 - T_1)}$$

$$\left(T_2 - T_1\right) \ln \theta = \ln\left(\frac{k_{T_2}}{k_{T_1}}\right) \qquad \ln \theta = \frac{1}{\left(T_2 - T_1\right)} \ln\left(\frac{k_{T_2}}{k_{T_1}}\right)$$

$$\theta = \left(\frac{k_{T_2}}{k_{T_1}}\right)^{\frac{1}{T_2 - T_1}} = 2^{\frac{1}{10}} = 1.072$$

24. $k = 0.22\ d^{-1}$, $\alpha = 0.008\ 5\ d^{-1}$

$$\frac{dC}{dt} = -\frac{k}{1 + \alpha t}, \quad \int_{C_0}^{C} \frac{dC}{C} = -k \int_0^t \frac{dt}{1 + \alpha t}$$

$$\ln\left(C/C_0\right) = -\frac{k}{\alpha} \ln\left(1 + \alpha t\right)\Big|_0^t$$

$$\ln\left(C/C_0\right) = -\frac{k}{\alpha} \ln\left(1 + \alpha t\right)$$

Taking the antilog of each side: $\frac{C}{C_0} = \left(1 + \alpha t\right)^{-k/\alpha}$

Substituting values for the coefficients: $\frac{C}{C_0} = \left(1 + 0.008\ 5t\right)^{-0.22/0.008\ 5} = \left(1 + 0.008\ 5t\right)^{-25.9}$

Data are given in the table below for times up to 10.0 days.

t, d	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0	8.0	10.0
C/C_0, %	89.6	80.3	72.0	64.6	58.0	52.1	42.1	34.0	27.6	18.2	12.1

25. Define S as solubility.

(a) $Mg_3(PO_4)_2$, $S = 6.1 \times 10^{-5}$ M

$3Mg^{2+} + 2\,PO_4^{3-} \rightarrow Mg_3(PO_4)_2$

$K_{sp} = (3S)^3(2S)^2 = 108S^5 = 108(6.1 \times 10^{-5})^5 = 9.12 \times 10^{-20}$

(b) FeS, $S = 6.3 \times 10^{-9}$ M

$Fe^{2+} + S^{2-} \rightarrow FeS$

$K_{sp} = (S)(S) = S^2 = (6.3 \times 10^{-9})^2 = 3.97 \times 10^{-17}$

(c) CuF_2, $S = 7.4 \times 10^{-3}$ M

$Cu^{2+} + 2F^- \rightarrow CuF_2$

$K_{sp} = (S)(2S)^2 = 4S^3 = 4(7.4 \times 10^{-3})^3 = 1.62 \times 10^{-6}$

26. The initial concentrations of $CaSO_4$ and Na_2CO_3 are:

$$CaSO_4{:}\quad \left(40\ \frac{mg}{L}\right)\left[\frac{1\ \text{mole}}{(40.1+32.1+4\times16.0)g}\right]\left(\frac{1\ g}{10^3\,mg}\right) = 2.94 \times 10^{-4}\ M$$

$$Na_2CO_3{:}\quad \left(100\ \frac{mg}{L}\right)\left[\frac{1\ \text{mole}}{(2\times23.1+12.0+3\times16.0)g}\right]\left(\frac{1\ g}{10^3\,mg}\right) = 9.42 \times 10^{-4}\ M$$

$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2+}$

x x x

The initial concentration of Ca^{2+} is 2.94×10^{-4} M

$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

x 2x x

The initial concentration of CO_3^{2-} is 9.42×10^{-4} M

At equilibrium,

$[Ca^{2+}][CO_3^{2-}] = 5.00 \times 10^{-9} = xy$ which corresponds to the reaction

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

z z z

$x = 2.94 \times 10^{-4} - z$; $y = 9.42 \times 10^{-4} - z$

$(2.94 \times 10^{-4} - z)(9.42 \times 10^{-4} - z) = 5.00 \times 10^{-9}$

$z^2 - 1.24 \times 10^{-3}\, z + 2.76 \times 10^{-7}$

$$z = \frac{1.24\times10^{-3} \pm \sqrt{1.54\times10^{-6} - 4(1)(2.76\times10^{-7})}}{2} = \frac{1.24\times10^{-3} \pm 6.60\times10^{-4}}{2}$$

$= 9.50 \times 10^{-4}$ M, 2.90×10^{-4} M

It is impossible for $z = 9.50 \times 10^{-4}$ M because the initial concentration of Ca^{2+} is lower than this value. Therefore the answer is 2.90×10^{-4} M. The final concentrations of the species are:

$[Ca^{2+}] = 2.94 \times 10^{-4} - 2.90 \times 10^{-4} = 4.0 \times 10^{-6}$ M

$[CO_3^{2-}] = 9.42 \times 10^{-4} - 2.90 \times 10^{-4} = 6.52 \times 10^{-4}$ M

27. The molar concentrations of Ca^{2+} and F^- are:

Ca^{2+}: $\left(150\ \frac{mg}{L}\right)\left[\frac{1\ mole}{40.1\ g}\right]\left(\frac{1\ g}{10^3\ mg}\right) = 3.74 \times 10^{-3}$ M

F^-: $\left(1\ \frac{mg}{L}\right)\left[\frac{1\ mole}{19.0\ g}\right]\left(\frac{1\ g}{10^3\ mg}\right) = 5.26 \times 10^{-5}$ M

The precipitation reaction is

$Ca^{2+} + 2\ F^- \rightarrow CaF_2$

x 2x x

$[Ca^{2+}][F^-]^2 = 3.00 \times 10^{-11}$

$x(2x)^2 = 4x^3 = 3.00 \times 10^{-11}$

If $[Ca^{2+}] = 3.74 \times 10^{-3}$ M

$$[F^-] = \sqrt{\frac{3.00 \times 10^{-11}}{[Ca^{2+}]}} = \sqrt{\frac{3.00 \times 10^{-11}}{3.74 \times 10^{-3}}} = 8.96 \times 10^{-5}\ M$$

The maximum amount of F^- is $\left(8.96 \times 10^{-5}\ \frac{M}{L}\right)\left(\frac{19\ 000\ mg}{mole}\right) = 1.70$ mg/L

If $[F^-] = 1.0$ mg/L

$$[Ca^{2+}] = \frac{3.00 \times 10^{-11}}{[F^-]^2} = \frac{3.00 \times 10^{-11}}{\left(5.26 \times 10^{-5}\right)^2} = 0.010\ 8\ M$$

The maximum amount of Ca^{2+} is

$$[Ca^{2+}] = \left(0.010\ 8\frac{M}{L}\right)\left(\frac{40\ 100\ mg}{mole}\right) = 435\ mg/L$$

27. A ligand is a set of atoms, ions, or molecules bonded to a central atom or ion in a complex.

28. free $[Hg^{2+}] = 0.10$ mg/L, free $[Cl^-] = 0.5$ mg/L

The MWs of Hg^{2+} and Cl^- are 200.6 and 35.45 g, respectively.

$$[Hg^{2+}] = \left(0.10\frac{mg}{L}\right)\left(\frac{1\ mole}{200.6\ g}\right)\left(\frac{1\ g}{1\ 000\ mg}\right) = 4.98 \times 10^{-7}\ M$$

$$[Hg^{2+}] = \left(0.50\frac{mg}{L}\right)\left(\frac{1\ mole}{35.45\ g}\right)\left(\frac{1\ g}{1\ 000\ mg}\right) = 1.41 \times 10^{-5}\ M$$

$Hg^{2+} + Cl^- \approx HgCl^+$ $K_1 = 8.8$

$HgCl^+ + Cl^- \approx HgCl_2$ $K_2 = 8.7$

$HgCl_2 + Cl^- \approx HgCl_3^-$ $K_3 = 1.0$

$HgCl_3^- + Cl^- \approx HgCl_4^{2-}$ $K_4 = 0.78$

$K_1 = \frac{[HgCl^+]}{[Hg^{2+}][Cl^-]}$ $[HgCl^+] = K_1[Hg^{2+}][Cl^-]$

$[HgCl^+] = 8.8(4.98 \times 10^{-7})(1.41 \times 10^{-5}) = 6.18 \times 10^{-11}$

$[HgCl_2] = K_2[HgCl^+][Cl^-] = 8.7(6.18 \times 10^{-11})(1.41 \times 10^{-5}) = 7.58 \times 10^{-15}$

$[HgCl_3^-] = K_3[HgCl_2][Cl^-] = 1.0(7.58 \times 10^{-15})(1.41 \times 10^{-5}) = 1.07 \times 10^{-19}$

$[HgCl_4^{2-}] = K_4[HgCl_3^-][Cl^-] = 0.78(1.07 \times 10^{-19})(1.41 \times 10^{-5}) = 1.18 \times 10^{-24}$

$\Sigma HgCl_i^{2-i} = 4.98 \times 10^{-7} + 6.18 \times 10^{-11} + 7.58 \times 10^{-15} + 1.07 \times 10^{-19} + 1.18 \times 10^{-24}$

$= 4.98 \times 10^{-7}$

29. Stability constant for $AgCl_3^{2-}$

$$\beta_3 = \frac{[AgCl_3^{2-}]}{[Ag^+][Cl^-]^3}$$

$$K_1 = \frac{[AgCl]}{[Ag^{2+}][Cl^-]},\ K_2 = \frac{[AgCl_2^-]}{[AgCl][Cl^-]},\ K_3 = \frac{[AgCl_3^{2-}]}{[AgCl_2^-][Cl^-]}$$

$K_1 = 3.45$, $K_2 = 2.22$, $K_3 = 0.33$

$\beta_3 = K_1K_2K_3 = (3.45)(2.22)(0.33) = 2.53$

30. 1 Bq = 27×10^{-9} Ci

For Ra-226, activity = 1 Ci/g.

For potassium-40, activity = 6.9×10^{-6} Ci/g

For cobalt-60, activity = 1.1×10^3 Ci/g

For cesium-137, activity = 87 Ci/g

For radon-222, activity = 1.6×10^5 Ci/g

Define M as the mass
A as the activity = 0.1 Bq
a as the specific activity

For radium-226: $M = \frac{A}{a} = (0.1\ \text{Bq})\left(\frac{27 \times 10^{-9}\ \text{Ci}}{1\ \text{Bq}}\right)\left(\frac{1\ \text{g}}{\text{Ci}}\right) = 2.7 \times 10^{-9}\ \text{g} = 2.7 \times 10^{-6}\ \text{mg}$

For potassium-40: $M = \frac{A}{a} = (0.1\ \text{Bq})\left(\frac{27 \times 10^{-9}\ \text{Ci}}{1\ \text{Bq}}\right)\left(\frac{1\ \text{g}}{6.9 \times 10^{-6}\ \text{Ci}}\right) = 3.91 \times 10^{-4}\ \text{g} = 0.391\ \text{mg}$

For cobalt-60: $M = \frac{A}{a} = (0.1\ \text{Bq})\left(\frac{27 \times 10^{-9}\ \text{Ci}}{1\ \text{Bq}}\right)\left(\frac{1\ \text{g}}{1.1 \times 10^{3}\ \text{Ci}}\right) = 2.45 \times 10^{-12}\ \text{g} = 2.45 \times 10^{-9}\ \text{mg}$

For cesium-137: $M = \frac{A}{a} = (0.1\ \text{Bq})\left(\frac{27 \times 10^{-9}\ \text{Ci}}{1\ \text{Bq}}\right)\left(\frac{1\ \text{g}}{87\ \text{Ci}}\right) = 3.10 \times 10^{-11}\ \text{g} = 3.10 \times 10^{-8}\ \text{mg}$

For radon-222: $M = \frac{A}{a} = (0.1\ \text{Bq})\left(\frac{27 \times 10^{-9}\ \text{Ci}}{1\ \text{Bq}}\right)\left(\frac{1\ \text{g}}{1.6 \times 10^{5}\ \text{Ci}}\right) = 1.69 \times 10^{-14}\ \text{g} = 1.69 \times 10^{-11}\ \text{mg}$

32. Radioactive decay of an unstable isotope generally does not terminate radiation because the daughter isotope(s) are usually unstable.

33. 1 g of uranium I decays for 1 000 yr, find radium formation

Uranium I decay: $\frac{dm_{UI}}{dt} = -k_{UI}m_{UI}$ $\quad \int_{m_{I0}}^{m_I} \frac{dm_{UI}}{m_{UI}} = -k_{UI}\int_0^t dt \quad \Rightarrow \quad m_{UI} = m_{UI0}e^{-k_{UI}t}$

$^{234}_{90}\text{Th}$ production and decay: $\frac{dm_{Th}}{dt} = f\left(\frac{dm_{Th}}{dt}\right)_{\text{production}} - \left(\frac{dm_{Th}}{dt}\right)_{\text{decay}}$

$$= f_1k_{UI}m_{UI} - k_{Th}m_{Th} = f_1k_{UI}m_{Ui0}e^{-k_{UI}t} - k_{Th}m_{Th}$$

$$\frac{dm_{Th}}{dt} + k_{Th}m_{Th} = fk_{UI}m_{UI0}e^{-k_{UI}t}$$

$$e^{k_{Th}t}\left(\frac{dm_{Th}}{dt} + k_{Th}m_{Th}\right) = \frac{d}{dt}\left(m_{Th}e^{k_{Th}t}\right)$$

$$\int d\left(m_{Th}e^{k_{Th}t}\right) = m_{Th}e^{k_{Th}t} = f_1k_{UI}m_{UI0}\int e^{(k_{Th}-k_{UI})t}dt = \frac{f_1k_{UI}m_{UI0}}{k_{Th}-k_{UI}}e^{(k_{Th}-k_{UI})t} + C$$

$$m_{Th} = \frac{f_1k_{UI}m_{UI0}}{k_{Th}-k_{UI}}e^{-k_{UI}t} + Ce^{-k_{Th}t}$$

The initial concentration of $^{234}_{90}\text{Th}$ = 0.

$$0 = \frac{f_1k_{UI}m_{UI0}}{k_{Th}-k_{UI}}e^{-k_{UI}(0)} + Ce^{-k_{Th}(0)} \quad \Rightarrow \quad C = -\frac{f_1k_{UI}m_{UI0}}{k_{Th}-k_{UI}}$$

$$m_{Th} = \frac{f_1k_{UI}m_{UI0}}{k_{Th}-k_{UI}}\left(e^{-k_{UI}t} - e^{-k_{Th}t}\right)$$

The developments for the other products follow the above procedure.

For $^{234}_{91}\text{Pa}^m$: $\frac{dm_{Pa}}{dt} = f_2k_{Th}m_{Th} - k_{Pa}m_{Pa} = \frac{f_1f_2k_{UI}k_{Th}m_{UI0}}{k_{Th}-k_{UI}}\left(e^{-k_{UI}t} - e^{-k_{Th}t}\right) - k_{Pa}m_{Pa}$

$$\frac{dm_{Pa}}{dt} + k_{Pa}m_{Pa} = \frac{f_1f_2k_{UI}m_{UI0}}{k_{Th}-k_{UI}}\left(e^{-k_{UI}t} - e^{-k_{Th}t}\right)$$

$$\int d\left(m_{Pa}e^{k_{Pa}t}\right) = m_{Pa}e^{k_{Pa}t} = \frac{f_1f_2k_{UI}k_{Th}m_{UI0}}{k_{Th}-k_{UI}}\left[\int e^{(k_{Pa}-k_{UI})t}dt - \int e^{(k_{Pa}-k_{Th})t}dt\right]$$

$$= \frac{f_1f_2k_{UI}k_{Th}m_{UI0}}{\left(k_{Th}-k_{UI}\right)}\left(\frac{1}{k_{Pa}-k_{Ui}} - \frac{1}{k_{Pa}-k_{Thi}}\right) + C$$

$$m_{Pa} = \frac{f_1f_2k_{UI}k_{Th}m_{UI0}}{\left(k_{Th}-k_{UI}\right)}\left(\frac{1}{k_{Pa}-k_{Ui}} - \frac{1}{k_{Pa}-k_{Thi}}\right)e^{-k_{Pa}t} + Ce^{-k_{Pa}t}$$

At t = 0, $m_{Pa} = 0$

$$0 = \frac{f_1 f_2 k_{UI} k_{Th} m_{UI0}}{\left(k_{Th} - k_{UI}\right)}\left(\frac{1}{k_{Pa} - k_{Ui}} - \frac{1}{k_{Pa} - k_{Thi}}\right) + C$$

$$C = -\frac{f_1 f_2 k_{UI} k_{Th} m_{UI0}}{\left(k_{Th} - k_{UI}\right)}\left(\frac{1}{k_{Pa} - k_{Ui}} - \frac{1}{k_{Pa} - k_{Thi}}\right)$$

$$m_{Pa} = \frac{f_1 f_2 k_{UI} k_{Th} m_{UI0}}{\left(k_{Th} - k_{UI}\right)}\left(\frac{1}{k_{Pa} - k_{Ui}} - \frac{1}{k_{Pa} - k_{Thi}}\right)\left(e^{-k_{Pa}t} - 1\right)$$

uranium I: $k_{UI} = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.51 \times 10^{9}\ \text{yr}} = 1.54 \times 10^{-10}\ \text{yr}^{-1}$

${}^{234}_{90}\text{Th}$: $k_{Th} = \frac{0.693}{t_{1/2}} = \frac{0.693}{24.1\ \text{d}} = 2.88 \times 10^{-2}\ \text{d}^{-1} = \left(2.88 \times 10^{-2}\ \text{d}^{-1}\right)\left(\frac{365\ \text{d}}{\text{yr}}\right) = 10.5\ \text{yr}^{-1}$

${}^{234}_{91}\text{Pa}^{m}$: $k_{Pa} = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.17\ \text{mo}} = 0.592\ \text{mo}^{-1} = \left(0.592\ \text{mo}^{-1}\right)\left(\frac{12\ \text{mo}}{\text{yr}}\right) = 7.11\ \text{yr}^{-1}$

$f_1 = 234/238 = 0.983$

$f_2 = 234/234 = 1.00$

$$m_{Pa} = \frac{f_1 f_2 k_{UI} k_{Th} m_{UI0}}{\left(k_{Th} - k_{UI}\right)}\left(\frac{1}{k_{Pa} - k_{Ui}} - \frac{1}{k_{Pa} - k_{Thi}}\right)\left(e^{-k_{Pa}t} - 1\right)$$

$$m_{Pa} = \frac{(0.983)(1.00)\left(1.54 \times 10^{-10}\ \text{yr}^{-1}\right)\left(10.5\ \text{yr}^{-1}\right)(1.0\ \text{g})}{\left(10.5\ \text{yr}^{-1} - 1.54 \times 10^{-10}\ \text{yr}^{-1}\right)}\left(\frac{1}{7.11\ \text{yr}^{-1} - 1.54 \times 10^{-10}\ \text{yr}^{-1}}\right.$$

$$\left. - \frac{1}{7.11\ \text{yr}^{-1} - 10.5\text{yr}^{-1}}\right)\left[e^{-\left(7.11\ \text{yr}^{-1}\right)\left(1\ 000\ \text{yr}\right)} - 1\right]$$

$$= 2.34 \times 10^{-11}\ \text{g}$$