Chapter 1

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

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

2.

Substance	MW	Concentration	mol in 1 L	mol 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	N 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 N	8.05

4. $$[\text{CO}] = (2.0\,\text{ppm})\left(\frac{1\,\text{mg}}{10^{6}\,\text{mg}}\Big/\text{ppm}\right)\left(\frac{1.2929\,\text{g air}}{\text{L}}\right)\left(\frac{10^{3}\,\text{mg}}{1\,\text{g}}\right)\left(\frac{10^{3}\,\text{L}}{1\,\text{m}^{3}}\right)\left(\frac{10^{3}\,\mu\text{g}}{\text{mg}}\right)$$

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

Solutions Manual to Accompany Theory and Practice of Water and Wastewater Treatment, Second Edition.
Ronald L. Droste and Ronald L. Gehr.

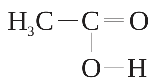
Companion website: www.wiley.com/go/droste/water

5. (a) NH_4^+ has a net charge of +1. Each H has an oxidation number of +1. $\therefore$ 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 number on each H is +1 for a total contribution of +4.

The oxidation number on each O is –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 oxidation number on each H is +1.

The oxidation number on each O is –2.

The average oxidation number on each C is

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

7. $NaClO_4$: Na - +1; O - –2; Ox. Number on Cl = 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

HCl: H - +1; x = –(1) = –1

NH_2Cl: Because Cl is more electronegative than N, it must have an oxidation number of –1 which is the case for all chloramines.

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

8. (a) First balance C, then H, and finally O.

$6H_2O + 6CO_2 \leftrightarrows C_6H_{12}O_6 + 6O_2$

(b) First balance Al, then SO_4^{2-}, then Ca, followed by, C, H, and O.

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

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. $NH_3 + O_2 \leftrightharpoons NO_3^-$

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

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

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

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

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.

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

(b) Oxidation reaction for ammonium.

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

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

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.

$O_2 + 4e^- \rightarrow 2O^{2-}$ (although O^{2-} does not exist on its own but this is the normal oxidation state of oxygen in compounds. Consider H_2O, for example.)

The equivalent weight is 32/4 = 8 g. Also reaction 25 in Table 1.3 can be checked to show that the equivalent weight of O_2 is 8 g.

11. Use reactions 22 and 24 from Table 1.3. Reverse reaction 22.

–Rxn 22: $\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O = \frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$

$\left(\frac{5}{8}\right)$Rxn 24: $\left(\frac{5}{8}\right)\left[\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O\right]$

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

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 23 and 24 in Table 1.3 to find a half-reaction for NO_2^- and NO_3^-.

Rxn 23: $\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}N_2 + \frac{2}{3}H_2O$

$$-\left(\frac{10}{6}\right)\text{Rxn 24:}\quad \tfrac{10}{6}\left(\tfrac{1}{10}N_2 + \tfrac{3}{5}H_2O = \tfrac{1}{5}NO_3^- + \tfrac{6}{5}H^+ + e^-\right) =$$

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

$$+\ \text{Rxn 23:}\quad \tfrac{1}{3}NO_2^- + \tfrac{4}{3}H^+ + e^- = \tfrac{1}{6}N_2 + \tfrac{2}{3}H_2O$$

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

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

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

$$\text{Rxn 8:}\quad \tfrac{1}{2}OCl^- + H^+ + e^- = \tfrac{1}{2}Cl^- + \tfrac{1}{2}H_2O$$

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

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 going to the right.

(b) 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 moving to the right.

14. (a) For a retardent reaction (destruction),

$$\frac{dC}{dt} = -\frac{k}{1+\alpha t}C$$

$$\int_{C_0}^{0.5C_0}\frac{dC}{C} = -k\int_0^{t_{1/2}}\frac{dt}{1+\alpha t}$$

$$\ln\ C\Big|_{C_0}^{0.5C_0} = -\frac{k}{\alpha}\ln\left(1+\alpha t\right)\Big|_0^{t_{1/2}}$$

$$\ln\ 0.5 = -\frac{k}{\alpha}\ln\left(1+\alpha t_{1/2}\right)$$

$$\frac{\alpha}{k}\ln\ 2 = \ln\left(1+\alpha t_{1/2}\right)$$

$$2^{\alpha/k} = 1 + \alpha t_{1/2}$$

$$t_{1/2} = \frac{1}{\alpha}\left(2^{\alpha/k} - 1\right)$$

Also

$$t_{1/2} = \frac{1}{\alpha}\left(e^{\frac{\alpha}{k}\ln 2} - 1\right) = \frac{1}{\alpha}\left(e^{\frac{0.693\alpha}{k}} - 1\right)$$

(b) Elementary autocatalytic reaction.

For the reaction: A + P $\rightarrow$ P + P

$C_T = C_{A0} + C_{P0}$, $C_T = C_A + C_P$

$$\frac{dC_A}{dt} = -k_1 C_A - k_2 C_A (C_T - C_A) = -k_1 C_A - k_2 C_A C_T + k_2 C_A^2$$

$$\int_{C_{A0}}^{0.5C_{A0}} \frac{dC_A}{\left(k_1 + k_2 C_T\right)C_A - k_2 C_A^2} = -\int_0^{t_{1/2}} dt = -t_{1/2}$$

$$-\left(\frac{1}{k_1 + k_2 C_T}\right)\ln\left(\frac{k_1 + k_2 C_T - k_2 C_A}{C_A}\right)\Bigg|_{C_{A0}}^{0.5C_{A0}} = -t_{1/2}$$

$$\left(\frac{1}{k_1 + k_2 C_T}\right)\left[\ln\left(\frac{k_1 + k_2 C_T - 0.5k_2 C_{A0}}{0.5C_{A0}}\right) - \ln\left(\frac{k_1 + k_2 C_T - k_2 C_{A0}}{C_{A0}}\right)\right] = t_{1/2}$$

$$\left(\frac{1}{k_1 + k_2 C_T}\right)\left[\ln\left(\frac{2k_1 + 2k_2 C_T - k_2 C_{A0}}{C_{A0}}\right) - \ln\left(\frac{k_1 + k_2 C_{P0}}{C_{A0}}\right)\right] = t_{1/2}$$

$$\left(\frac{1}{k_1 + k_2 C_T}\right)\ln\left(\frac{2k_1 + 2k_2 C_T - k_2 C_{A0}}{k_1 + k_2 C_{P0}}\right) = t_{1/2}$$

$$t_{1/2} = \left(\frac{1}{k_1 + k_2 C_T}\right)\ln\left(\frac{2k_1 + k_2 C_T + k_2 C_T - k_2 C_{A0}}{k_1 + k_2 C_{P0}}\right) = \left(\frac{1}{k_1 + k_2 C_T}\right)\ln\left(\frac{2k_1 + k_2 C_T + k_2 C_{P0}}{k_1 + k_2 C_{P0}}\right)$$

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15. From Eq. (1.9) $\mu = 1.6 \times 10^{-5}\ \kappa$

From Eq. (1.8) $\mu = 2.5 \times 10^{-5}$ (TDS)

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

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

where TDS is in mg/L
κ is in μmhos/cm

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16. Eq. (1.27): $k = A \exp\left(-\frac{E_a}{RT}\right)$ Eq. (1.28): $k_{T_2} = k_{T_1}\theta^{(T_2 - T_1)}$

From Eq. (1.27),

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

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

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17. $p = 0.21$ atm, $T = 25°\text{C} = 25° + 273.2° = 298.2°\text{K}$

$pV = n\mathrm{R}T$

R = 0.082 L-atm/°-mol

$$\frac{n}{V} = \frac{p}{\mathrm{R}T} = \frac{0.21\text{ atm}}{\left(0.082\text{ L-atm/°-mol}\right)\left(298.2°\right)} = 8.59 \times 10^{-3}\text{ M}$$

$$= \left(8.59\times10^{-3}\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{32\text{ g}}{\text{mol}}\right)\left(\frac{1000\text{ mg}}{\text{g}}\right) = 275\text{ mg/L}$$

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

$pV = n\mathrm{R}T$

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

R = 0.082 L-atm/°-mol

for O_2: $$\frac{n}{V} = \frac{p}{\mathrm{R}T} = \frac{0.21\text{ atm}}{\left(0.082\text{ L-atm/°-mol}\right)\left(298.2°\right)} = 8.59 \times 10^{-3}\text{ M}$$

$$= \left(8.59\times10^{-3}\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{32\text{ g}}{\text{mol}}\right) = 0.275\text{ g/L}$$

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

for N_2: $$\frac{n}{V} = \frac{p}{\mathrm{R}T} = \frac{0.79\text{ atm}}{\left(0.082\text{ L-atm/°-mol}\right)\left(298.2°\right)} = 0.032\,3\text{ M}$$

$$= \left(0.0323\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{28\text{ g}}{\text{mol}}\right) = 0.904\text{ g/L}$$

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.)

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19. (a) $T = 25°\text{C}$, $p_T = 1$ atm

From Henry's law:

$[\text{G(aq)}] = C_s = K_H[\text{G(g)}] = K_H p_{N2}$ (C_s is saturation concentration)

At 25°C = 298°K for N_2, from Table 1.4: $K_H = 18.2$ mg/L-atm

From Dalton's law:

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

$[N_2]$ = $\left(18.2\dfrac{\text{mg N}_2}{\text{L - atm}}\right)(0.79\,\text{atm})$ = 14.4 mg N/L

(b) T = 5°C, p_T = 1 atm

T = 5°C = 278°K. From Table 1.4, $\Delta H^o/R$ = 1600

$$K_{H,T2} = K_{H,T1}\exp\left[\frac{\Delta H^o}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right] = \left(18.2\ \frac{\text{mg/L}}{\text{atm}}\right)\exp\left[(1600)\left(\frac{1}{278}-\frac{1}{298}\right)\right]$$

= 26.8 mg/L-atm

$[N_2]$ = $\left(26.8\dfrac{\text{mg N}_2}{\text{L - atm}}\right)(0.79\,\text{atm})$ = 21.2 mg N/L

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20. Determine the Henry's law constant for this situation in the following units. (a) mg/L water/O_2 pressure (atm); (b) (mg/L water)/mg/L (air); (c) mol fraction in water/mol fraction (in air; (d) mg/L water/O_2 pressure (bar); (e) mol/L water/O_2 pressure (Pa).

For (a): The partial pressure of O_2 = (0.21)(1 atm) = 0.21 atm

K_H = $\dfrac{10.78\,\dfrac{\text{mg}}{\text{L}}}{0.21\text{atm}}$ = 51.3 mg/L-atm

For (b): The concentration of oxygen in the air is determined from the universal gas law. $pV = n\text{R}T$.

T = 273 + 12 = 285°K, R = 0.082 054 L-atm/deg-mol

$$\frac{n_{O_2}}{V} = \frac{p_{O_2}}{RT} = \frac{0.21\text{atm}}{\left(0.082054\dfrac{\text{L - atm}}{{}^o\text{K - mol}}\right)(285^o\,\text{K})} = 0.008\ 98\ \text{mol/L}$$

$[O_2(g)]$ = $\left(0.00898\dfrac{\text{mol}}{\text{L}}\right)\left(\dfrac{32\,\text{g O}_2}{\text{mol}}\right)\left(\dfrac{1000\text{mg}}{\text{g}}\right)$ = 287 mg/L

K_H = $\dfrac{10.78\,\dfrac{\text{mg}}{\text{L}}}{287\,\dfrac{\text{mg}}{\text{L}}}$ = 0.0376 mg/L/(mg/L)

For (c): At 12°C, $\rho_w = 999.7 - \dfrac{2(999.7-999.1)}{5}$ = 999.5 g/L

In water, the number of moles of water is $\dfrac{999.5\,\dfrac{\text{g}}{\text{L}}}{18\,\dfrac{\text{g}}{\text{mol}}}$ = 55.53 mol/L

The number of moles of oxygen (and other dissolved entities) in 1 L of typical freshwater is insignificant compared *to* the number of moles of water; thus n = 55.53 mol.

The mole fraction of oxygen dissolved in 1 L of water is

$$\frac{\left(10.78\,\frac{\text{mg}}{\text{L}}\right)\left(\frac{1\,\text{mol}}{32\,000\,\text{mg}}\right)}{55.53\,\text{mol/L}} = 6.067 \times 10^{-6}$$

From Section 1.9, the mole fraction of a gas in a mixture of gases is

$p_i = \dfrac{n_i}{n} p_T$ (p_T is total atmospheric pressure)

The partial pressure of nitrogen = (0.79)(1 atm) = 0.79 atm

$$\frac{n_{N_2}}{V} = \frac{p_{N_2}}{RT} = \frac{0.79\,\text{atm}}{\left(0.082054\,\frac{\text{L - atm}}{^{o}\text{K - mol}}\right)\left(285^{o}\,\text{K}\right)} = 0.0338 \text{ mol/L}$$

The total number of moles in 1 L of the gas phase is 0.008 98 + 0.033 8 = 0.042 8

The mol fraction of O_2 in the gas phase is

$p_T(0.008\,98)/(0.0428) = 0.210p_T$

$K_H = \dfrac{6.067\times10^{-6}}{0.210p_T} = 2.889 \times 10^{-5}/p_T$ (where p_T is in atm)

(Note: when K_H is expressed on a mol fraction/mol fraction basis, p_T is usually not expressed and assumed to be 1 atm.)

For (d): $p_{O2} = (0.21\,\text{atm})\left(\dfrac{1.013\,\text{bar}}{1\,\text{atm}}\right) = 0.213$ bar

$$K_H = \frac{10.78\,\frac{\text{mg}}{\text{L}}}{0.213\,\text{bar}} = 50.6 \text{ mg/L-bar}$$

For (e): $p_{O2} = (0.21\,\text{atm})\left(\dfrac{101.3\,\text{kPa}}{1\,\text{atm}}\right) = 21.3$ kPa

$$[O_2(aq)] = \left(10.78\,\frac{\text{mg}}{\text{L}}\right)\left(\frac{1\,\text{mol}}{32\,000\,\text{mg}}\right) = 3.369 \times 10^{-4} \text{ mol/L}$$

$$K_H = \frac{3.369\times10^{-4}\,\frac{\text{mol}}{\text{L}}}{21.3\,\text{kPa}}\left(\frac{1\,\text{kPa}}{1000\,\text{Pa}}\right) = 1.582 \times 10^{-8} \text{ mol/L-Pa}$$

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21. The depth is 100 m and atmospheric air contains oxygen at 0.21 atm. Ignore the depletion of oxygen in the air.

$[G(aq)] = C_s = K_H[G(g)] = K_H p_{O2}$ (C_s is saturation concentration)

From Table 1.4, $K_H = 38.9$ mg/L-atm

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

p_0 = atmospheric pressure = 101.3 kN/m^2 = 101.3×10^3 kg/m-s^2

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

g = 9.81 m/s^2

The total pressure at a depth of 100 m is

p_T = 101.3 × 10^3 + (997.0 kg/m^3)(9.81 m/s^2)(100 m) = 101.3 × 10^3 + 978.1 × 10^3 kg/m-s^2

$$= 1079.4 \times 10^3 \text{ kg/m-s}^2 = \left(1079.4\times10^3 \frac{\text{kg}}{\text{m - s}^2}\right)\left(\frac{1\,\text{atm}}{101.3\times10^3 \frac{\text{kg}}{\text{m - s}^2}}\right) = 10.66 \text{ atm}$$

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

$$p_{O2} = \frac{n_1}{n_2} p_T = 0.21(1079.4 \times 10^3 \text{ kg/m-s}^2) = 226.7 \times 10^3 \text{ kg/m-s}^2$$

$$= 2.24 \text{ atm}$$

$$[O_2] = \left(38.9 \frac{\text{mg}\,O_2}{\text{L - atm}}\right)\left(2.24\,\text{atm}\,O_2\right)$$

$$= 87.1 \text{ mg } O_2/\text{L}$$

This is the highest saturation concentration possible due to the assumption that no oxygen was transferred from an air bubble. Solving the actual situation is fairly complex since pressure varies with column depth, nitrogen is transferred into and out of the liquid (which affects the concentration of oxygen in a bubble) and, of course, oxygen is consumed by microorganisms.

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

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

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

θ = 1.06, at 30°C

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

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

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

$$-\frac{1}{C}\bigg|_{C_O}^{C} = -kt, \qquad \frac{1}{C_O} - \frac{1}{C} = -kt$$

$$\frac{1}{C} = \frac{1}{C_O} + kt, \qquad C = \frac{C_O}{1 + C_O kt}$$

$$C = \frac{2.6\times10^{-4} \text{ mol/L}}{1+\left(2.6\times10^{-4} \text{ mol/L}\right)\left(106.8 \text{ L/mol/h}\right)\left(2 \text{ h}\right)} = 2.46 \times 10^{-4} \text{ M}$$

θ = 1.062, at 30°C

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

$$C = \frac{2.6\times10^{-4}\ \text{mol/L}}{1+\left(2.6\times10^{-4}\ \text{mol/L}\right)\left(355.7\ \text{L/mol/h}\right)\left(2\ \text{h}\right)} = 2.19\times10^{-4}\ \text{M}$$

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

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

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

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

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

24. k = 0.22 d^{-1}, α = 0.008 5 d^{-1}

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

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

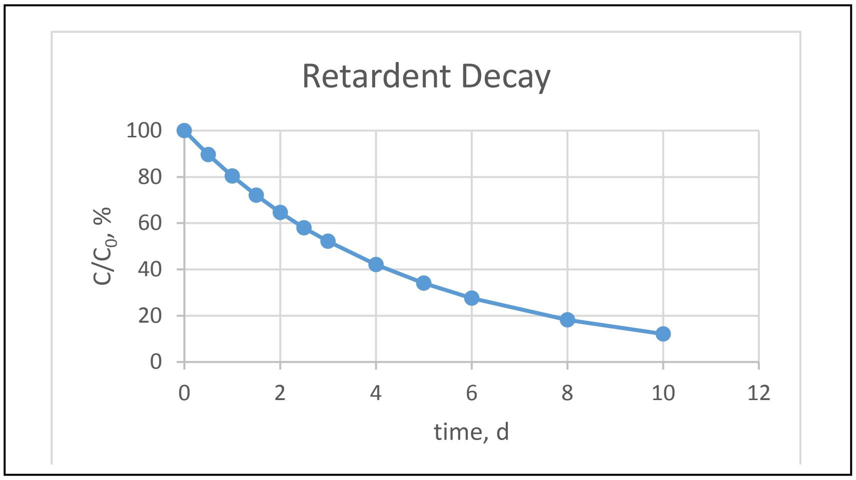
$$\ln\ \left(C/C_0\right) = -\frac{k}{\alpha}\ \ln\ \left(1+\alpha t\right)$$

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

Substituting values for the coefficients: $\frac{C}{C_0} = \left(1+0.0085t\right)^{-0.22/0.0085} = \left(1+0.0085t\right)^{-25.9}$

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. $$\frac{dC}{dt} = -\frac{kC^{0.70}}{(K+C)^{0.5}}$$ C- mg/L, t - h

(a) To be dimensionally consistent, the units on K are mg/L; for k:

$$\frac{\text{mg}}{\text{L}-\text{h}} = \frac{k\left(\frac{\text{mg}}{\text{L}}\right)^{0.7}}{\left(\frac{\text{mg}}{\text{L}}\right)^{0.5}} = k\left(\frac{mg}{L}\right)^{0.2} \Rightarrow k \text{ has units of } (\text{mg/L})^{0.8}\text{h}^{-1}$$

(b) $K << C$

$$\frac{dC}{dt} = -\frac{kC^{0.70}}{(K+C)^{0.5}} \approx \frac{kC^{0.70}}{C^{0.5}} = kC^{0.2}$$

The order of the reaction is 0.2.

26. Define S as solubility.

(a) $Mg_3(PO_4)_2$, S = 6.1×10^{-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

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

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

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

CaSO$_4$: $\left(40\ \frac{\text{mg}}{\text{L}}\right)\left[\frac{1\ \text{mol}}{(40.1+32.1+4\times16.0)\,\text{g}}\right]\left(\frac{1\ \text{g}}{10^3\text{mg}}\right)$ = 2.94×10^{-4} M

Na$_2$CO$_3$: $\left(100\ \frac{\text{mg}}{\text{L}}\right)\left[\frac{1\ \text{mol}}{(2\times23.1+12.0+3\times16.0)\,\text{g}}\right]\left(\frac{1\ \text{g}}{10^3\text{mg}}\right)$ = 9.42×10^{-4} M

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

$x \quad\quad x \quad\quad x$

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

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

$y \quad\quad 2y \quad\quad y$

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

At equilibrium,

$[Ca^{2+}][CO_3^{2-}] = 3.36 \times 10^{-9} = xy$ which corresponds to the reaction

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

$z \quad\quad z \quad\quad z$

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

$(2.94 \times 10^{-4} - z)(9.42 \times 10^{-4} - z) = 3.36 \times 10^{-9}$

$z^2 - 1.24 \times 10^{-3}\, z + 2.74 \times 10^{-7}$

$$z = \frac{1.24\times10^{-3} \pm \sqrt{1.54\times10^{-6} - 4(1)(2.74\times10^{-7})}}{2} = \frac{1.24\times10^{-3} \pm 6.60\times10^{-4}}{2}$$

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

It is impossible for z = 9.50×10^{-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

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

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

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

The precipitation reaction is

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

$x \quad\quad 2x \quad\quad x$

$[Ca^{2+}][F^-]^2 = 3.45 \times 10^{-11}$

$x(2x)^2 = 4x^3 = 3.45 \times 10^{-11}$

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

$$[F^-] = \sqrt{\frac{3.45\times10^{-11}}{[Ca^{2+}]}} = \sqrt{\frac{3.45\times10^{-11}}{3.74\times10^{-3}}} = 9.60 \times 10^{-5}\ \text{M}$$

The maximum amount of F^- is $\left(9.60\times10^{-5}\ \frac{\text{M}}{\text{L}}\right)\left(\frac{19\ 000\ \text{mg}}{\text{mol}}\right) = 1.83$ mg/L

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

$$[Ca^{2+}] = \frac{3.45\times10^{-11}}{[F^-]^2} = \frac{3.45\times10^{-11}}{(5.26\times10^{-5})^2} = 0.012\ 5\ \text{M}$$

The maximum amount of Ca^{2+} is

$$[Ca^{2+}] = \left(0.0125\frac{\text{mol}}{\text{L}}\right)\left(\frac{40100\,\text{mg}}{\text{mol}}\right) = 503\ \text{mg/L}$$

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

30. 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.

$$[Hg^{2+}] = \left(0.10\frac{\text{mg}}{\text{L}}\right)\left(\frac{1\ \text{mol}}{200.6\ \text{g}}\right)\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right) = 4.98 \times 10^{-7}\ \text{M}$$

$$[Cl^-] = \left(0.50\frac{\text{mg}}{\text{L}}\right)\left(\frac{1\ \text{mol}}{35.45\ \text{g}}\right)\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right) = 1.41 \times 10^{-5}\ \text{M}$$

$Hg^{2+} + Cl^- \leftrightharpoons HgCl^+$ $\quad K_1 = 7.33$

$HgCl^+ + Cl^- \leftrightharpoons HgCl_2$ $\quad K_2 = 6.70$

$HgCl_2 + Cl^- \leftrightharpoons HgCl_3^-$ $\quad K_3 = 1.0$

$HgCl_3^- + Cl^- \leftrightharpoons HgCl_4^{2-}$ $\quad K_4 = 0.60$

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

$[HgCl^+] = 7.33(4.98 \times 10^{-7})(1.41 \times 10^{-5}) = 5.15 \times 10^{-11}$

$[HgCl_2] = K_2[HgCl^+][Cl^-] = 6.70(5.15 \times 10^{-11})(1.41 \times 10^{-5}) = 4.87 \times 10^{-15}$

$[HgCl_3^-] = K_3[HgCl_2][Cl^-] = 1.0(4.87 \times 10^{-15})(1.41 \times 10^{-5}) = 6.86 \times 10^{-20}$

$[HgCl_4^{2-}] = K_4[HgCl_3^-][Cl^-] = 0.60(6.86 \times 10^{-20})(1.41 \times 10^{-5}) = 5.80 \times 10^{-25}$

$$\Sigma HgCl_i^{2-i} = 4.98 \times 10^{-7} + 5.15 \times 10^{-11} + 4.87 \times 10^{-15} + 6.86 \times 10^{-20} + 5.80 \times 10^{-25}$$

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

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

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

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

$K_1 = 3.30$, $K_2 = 1.30$, $K_3 = 0.36$

$\beta_3 = K_1K_2K_3 = (3.30)(1.30)(0.36) = 1.54$

32. 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: $M = \frac{A}{a} = (0.1\text{ Bq})\left(\frac{27\times10^{-9}\text{Ci}}{1\text{ Bq}}\right)\left(\frac{1\text{ g}}{\text{Ci}}\right) = 2.7 \times 10^{-9}\text{ g} = 2.7 \times 10^{-6}\text{ mg}$

For potassium-40: $M = \frac{A}{a} = (0.1\text{ Bq})\left(\frac{27\times10^{-9}\text{Ci}}{1\text{ Bq}}\right)\left(\frac{1\text{ g}}{6.9\times10^{-6}\text{Ci}}\right) = 3.91 \times 10^{-4}\text{ g} = 0.391\text{ mg}$

For cobalt-60: $M = \frac{A}{a} = (0.1\text{ Bq})\left(\frac{27\times10^{-9}\text{Ci}}{1\text{ Bq}}\right)\left(\frac{1\text{ g}}{1.1\times10^{3}\text{Ci}}\right) = 2.45 \times 10^{-12}\text{ g} = 2.45 \times 10^{-9}\text{ mg}$

For cesium-137: $M = \frac{A}{a} = (0.1\text{ Bq})\left(\frac{27\times10^{-9}\text{Ci}}{1\text{ Bq}}\right)\left(\frac{1\text{ g}}{87\text{ Ci}}\right) = 3.10 \times 10^{-11}\text{ g} = 3.10 \times 10^{-8}\text{ mg}$

For radon-222: $M = \frac{A}{a} = (0.1\text{ Bq})\left(\frac{27\times10^{-9}\text{Ci}}{1\text{ Bq}}\right)\left(\frac{1\text{ g}}{1.6\times10^{5}\text{Ci}}\right) = 1.69 \times 10^{-14}\text{ g} = 1.69 \times 10^{-11}\text{ mg}$

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