Solutions Manual

to accompany

Environmental Engineering Science

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William W Nazaroff
Lisa Alvarez-Cohen
October 10, 2000

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Chapter 1

$\boxed{1.1}$

(a) In water "ppb" refers to a mass fraction:

$$\text{ppb (water)} = \frac{\text{mass of contaminant} \times 10^9}{\text{mass of (water + contaminant)}}$$

In air "ppb" refers to a mole or, equivalently, volume fraction:

$$\text{ppb(air)} = \frac{\text{moles (or volume) of contaminant} \times 10^9}{\text{moles (or volume) of (air + contaminant)}}$$

Since the mass and moles of a contaminant are usually much lower than the mass of water and moles of air, respectively, the contaminant is usually left out of the denominator.

(b) 35 ppm is equal to $\frac{35 \times 10^{-6} \text{ moles CO}}{\text{mole air}}$

To convert this to a mass concentration, we first need to determine what volume is taken up by 1 mole of air. We can use the IDEAL GAS LAW:

$$PV = nRT \; ; \; \frac{V}{n} = \frac{RT}{P}$$

Assuming $P = 1$ atm and $T = 293$ K, and using $R = 82.05 \times 10^{-6} \frac{\text{atm m}^3}{\text{mol K}}$:

$$\frac{V}{n} = \frac{(82.05 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1})(293 \text{ K})}{1 \text{ atm}}$$

$$= 0.024 \text{ m}^3 \text{ mol}^{-1}$$

We also need to know what mass is contained in 1 mole of CO:

$$MW_{CO} = 12 \text{ g mol}^{-1} + 16 \text{ g mol}^{-1} = 28 \text{ g mol}^{-1}$$

Thus, the conversion is:

$$\left(\frac{35 \times 10^{-6} \text{ mol CO}}{\text{mol air}}\right)\left(\frac{28 \text{ g CO}}{\text{mol}}\right)\left(10^3 \frac{\text{mg}}{\text{g}}\right)\left(\frac{1 \text{ mol air}}{0.024 \text{ m}^3 \text{ air}}\right)$$

$$= \boxed{41 \text{ mg m}^{-3}}$$

(c) The conversion is:

$$\left(\frac{0.005 \text{ mg Cd}}{\text{L H}_2\text{O}}\right)\left(\frac{1 \text{ L H}_2\text{O}}{1000 \text{ g H}_2\text{O}}\right)\left(\frac{1 \text{ g Cd}}{10^3 \text{ mg Cd}}\right)\underbrace{(10^6)}_{\text{to convert to ppm}} = \boxed{0.005 \text{ ppm}}$$

1.2

(a) As in problem 1.1(b) above, we use the ideal gas law and the molecular weight of the contaminant, in this case $CHCl_3$, to make the conversion. Recall:

$$PV = nRT \; ; \; \frac{V}{n} = \frac{RT}{P}$$

With $P = 1$ atm and $T = 293$ K, and using $R = 82.05 \times 10^{-6} \frac{\text{atm m}^3}{\text{mol K}}$

$$\frac{V}{n} = \frac{(82.05 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1} \text{K}^{-1})(293 \text{ K})}{1 \text{ atm}}$$
$$= 0.024 \text{ m}^3 \text{ mol}^{-1}$$

The molecular weight of $CHCl_3$ is:

$$MW_{CHCl_3} = 12 \text{ g mol}^{-1} + 1 \text{ g mol}^{-1} + 3(35.5 \text{ g mol}^{-1})$$
$$= 119.5 \text{ g mol}^{-1}$$

The conversion is:

$$\left(\frac{0.4 \; \mu g \; CHCl_3}{m^3 \text{ air}}\right)\left(\frac{0.024 \; m^3 \text{ air}}{\text{mol air}}\right)\left(\frac{1 \text{ g}}{10^6 \; \mu g}\right)\left(\frac{1 \text{ mol } CHCl_3}{119.5 \text{ g } CHCl_3}\right)(10^9)$$
$$= \boxed{0.08 \text{ ppb } CHCl_3}$$

(b) We use the fact that the density of water is 1 g/mL to make the conversion:

$$\left(\frac{42 \; \mu g \; CHCl_3}{L \; H_2O}\right)\left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right)\left(\frac{1 \text{ mL } H_2O}{g \; H_2O}\right)\left(\frac{1 \text{ g}}{10^6 \; \mu g}\right)(10^9)$$
$$= \boxed{42 \text{ ppb } CHCl_3}$$

(c) The exposures to $CHCl_3$ through inhalation and ingestion:

	Inhalation	Ingestion
Amount consumed	20 m^3 day^{-1}	2 L day^{-1}
$CHCl_3$ concentration	0.4 μg m^{-3}	42 μg L^{-1}
$CHCl_3$ exposure	8 μg day^{-1}	84 μg day^{-1}

1.2 (continued)

(d) The exposures to C_2Cl_4 through inhalation and ingestion:

	Inhalation	Ingestion
Amount consumed	$20\ m^3\ day^{-1}$	$2\ L\ day^{-1}$
C_2Cl_4 concentration	$2.1\ \mu g\ m^{-3}$	$0.10\ \mu g\ L^{-1}$
C_2Cl_4 exposure	$\boxed{42\ \mu g\ day^{-1}}$	$\boxed{0.20\ \mu g\ day^{-1}}$

(e) Ingestion is more important than inhalation for chloroform (by a factor of 10), while inhalation is more important for C_2Cl_4.

1.3

(a) The conversion in water is:

$$\left(\frac{80\times10^{-9}\ g\ C_2H_3Cl}{g\ H_2O}\right)\left(\frac{10^6\ \mu g}{g}\right)\left(\frac{10^3\ g}{kg}\right)\left(\frac{1\ kg\ H_2O}{L\ H_2O}\right)$$

$$= \boxed{80\ \mu g\ L^{-1}\ C_2H_3Cl}$$

Note: In general, $[ppb] = \left[\frac{\mu g}{L}\right]$ in water.

(b) The conversion in air is:

$$\left(\frac{80\times10^{-9}\ mol\ C_2H_3Cl}{mol\ air}\right)\left(\frac{62.5\ g\ C_2H_3Cl}{mol}\right)\left(\frac{10^6\ \mu g}{g}\right)\left(\frac{1\ mol\ air}{0.024\ m^3}\right)\left(\frac{1 m^3}{10^3 L}\right.$$

$$= \boxed{0.2\ \mu g\ L^{-1}\ C_2H_3Cl}$$

Note: See problems 1.1 and 1.2 for a calculation of what volume is occupied by a mole of air. $P = 1$ atm and $T = 293$ K are assumed.

1.4

We want to convert mass concentration to molarity and normality for five ions in drinking water. Recall that the definitions of molarity and normality are as follows:

$$\text{MOLARITY} = M = \frac{\#\text{ of moles of solute}}{\text{volume of solution}} - \left[\frac{mol}{L}\right]$$

$\boxed{1.4}$ (continued)

$$\text{NORMALITY} = N = \frac{\#\text{ of equivalents of solute}}{\text{volume of solution}} = \frac{eq.}{L}$$

where

$$eq. = |\text{net charge}| \times \text{moles}$$

Therefore

$$N = |\text{net charge}| \times M$$

Our conversions are as follows:

Species	Mass Concentration ($mg\ L^{-1}$)	Atomic Weight ($g\ mole^{-1}$)	Net Charge	M ($mol\ L^{-1}$)	N ($eq\ L^{-1}$)
Fe^{3+}	0.02	56	3	3.6×10^{-7}	1.1×10^{-6}
Ca^{2+}	9.8	40	2	2.5×10^{-4}	4.9×10^{-4}
Mg^{2+}	1.8	24	2	7.5×10^{-5}	1.5×10^{-4}
K^{+}	0.6	39	1	1.5×10^{-5}	1.5×10^{-5}
Na^{+}	4.6	23	1	2.0×10^{-4}	2.0×10^{-4}

$\boxed{1.5}$

We first want to find the total mass of CO_2 in the atmosphere, given:

$$M_{atm} = 5.1 \times 10^{18}\ kg$$
$$Y_{CO_2} = 350\ ppm$$

We also know that

$$MW_{air} = 28.9\ g\ mole^{-1}$$
$$MW_{CO_2} = 44\ g\ mole^{-1}$$

Therefore, the total mass of CO_2 is:

$$M_{CO_2} = \left(\frac{350\ mol\ CO_2}{10^6\ mol\ air}\right)\left(\frac{1\ mole\ air}{29.8\ g}\right)\left(\frac{10^3 g}{kg}\right)\left(5.1 \times 10^{18}\ kg\ air\right)$$

$$M_{CO_2} = \left(6.18 \times 10^{16}\ mol\ CO_2\right)\left(\frac{44\ g\ CO_2}{mol\ CO_2}\right)\left(\frac{1\ metric\ tons}{10^6\ g}\right)$$

$$M_{CO_2} = 2.72 \times 10^{16}\ metric\ tons$$

The rate of mass accumulation, then, is:

$$Rate = \left(2.72 \times 10^{16}\ metric\ tons\right)\left(0.5\ \frac{\%}{year}\right) = \boxed{1.4 \times 10^{10}\ \frac{metric\ tons}{year}}$$

1.6

(a) To find the CO_2 emission rate from private automobiles in the US, simply multiply:

$$\left(1.2\times10^{8}\,\text{cars}\right)\left(\frac{10^{4}\,\text{miles}}{\text{car yr}}\right)\left(\frac{1\,\text{gal}\,C_8H_{18}}{18\,\text{miles}}\right)\left(\frac{3785\,\text{cm}^3\,C_8H_{18}}{\text{gal}\,C_8H_{18}}\right)$$

$$\times\left(\frac{0.72\,\text{g}\,C_8H_{18}}{1\,\text{cm}^3\,C_8H_{18}}\right)\left(\frac{96\,\text{g}C}{114\,\text{g}\,C_8H_{18}}\right)\left(\frac{44\,\text{g}\,CO_2}{12\,\text{g}C}\right)\left(\frac{1\ \text{metric tonne}}{10^{6}\,\text{g}}\right)$$

$$=\boxed{5.6\times10^{8}\ \frac{\text{metric tonnes}\ CO_2}{\text{yr}}}$$

(b) Of the total mass accumulation of CO_2 in the atmosphere, US private automobiles account for $\frac{5.6\times10^{8}}{1.4\times10^{10}}\times100=\underline{4}\,\%$. Thus, if US auto CO_2 emissions were reduced to 0 through regulation, global CO_2 mass accumulation would still be 96% of our current estimates. However automobiles worldwide may also be significant contributers to CO_2 accumulation, and so fuel efficiency regulations may reduce emissions.

1.7

First we want to find out how much PCE waste is produced each month:

$$\frac{\text{PCE waste produced}}{\text{month}}=\frac{\text{PCE purchased}}{\text{month}}(1-0.3)$$

$$=\frac{250\ \text{L}}{\text{month}}(0.7)=175\ \frac{\text{L PCE}}{\text{month}}$$

Now find out how long for the 0.7 m³ (= 700 L) disposal container to fill:

$$\tau=\frac{700\ \text{L}}{175\ \text{L/month}}=\boxed{4\ \text{months}}$$

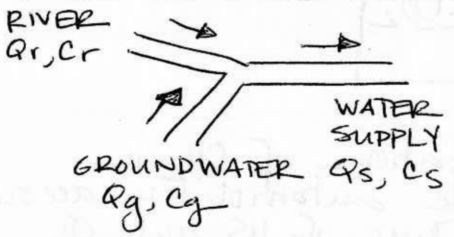
container will have to be emptied this often

$\boxed{1.8}$

We want to determine the relative amounts of river water and groundwater to be used for Ecocity's water supply, given the following:

Barium drinking water standard = 2 mg L^{-1}
Barium concentrantion in river = 0.5 mg L^{-1}
Barium concentration in groundwater = 9 mg L^{-1}
Water supply needs for Ecocity = 10 m^3 day^{-1}

We can use the mass balance concept to solve:



Let $Q_s = 10\ m^3\ day^{-1}$
$C_s = 5\ mg\ L^{-1}$
$C_r = 1.5\ mg\ L^{-1}$
$C_g = 9\ mg\ L^{-1}$

Mass balance on water: $Q_r + Q_g = Q_s$
Mass balance on barium: $C_r Q_r + C_g Q_g = C_s Q_s$
Therefore:

$$Q_r + Q_g = 10\ m^3\ day^{-1}$$

$$(0.5\ mg L^{-1}) Q_r + (9\ mg L^{-1}) Q_g = (2 mg\ L^{-1})(10\ m^3 d^{-1})$$

Setting $Q_r = 10 - Q_g$, substituting into the second equation and solving for Q_g:

$$0.5(10 - Q_g) + 9 Q_g = 20$$

$$5 - 0.5 Q_g + 9 Q_g = 20$$

$$8.5 Q_g = 15$$

$$Q_g = 1.76\ m^3\ d^{-1}$$

and $Q_r = 10 - Q_g = 8.24\ m^3\ d^{-1}$

So Ecocity should use:

1.8 $m^3 d^{-1}$	(47%)	groundwater
8.2 $m^3 d^{-1}$	(53%)	river water

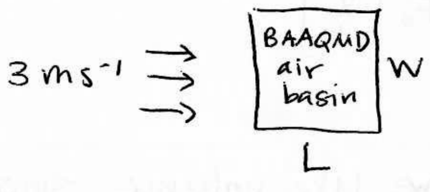
Note: We can check to make sure this combination of flows will give us the desired barium concentration:

$$C_s = \frac{0.5 \times 8.2 + 9 \times 1.8}{10} = 2.0\ \frac{mg}{L}\ ✓$$

$\boxed{1.9}$

(a) We want to find the characteristic residence time of air in the BAAQMD air basin, given that the basin encompasses 6094 mi^2 and a steady wind of 3 $m s^{-1}$ blows from the west.

Consider a generic rectangular air basin:



Let's start with the simplest case, with L=W:

$$L = \sqrt{6094} = 78.06 \text{ miles}$$
$$L = (78.06 \text{ miles})(1609 \text{ m mile}^{-1}) = 125600 \text{m}$$

Thus, the residence time is:

$$\tau = \frac{125600 \text{ m}}{3 \text{ m s}^{-1}} = 41900 \text{ s}$$
$$\tau = (41900 \text{ s})\left(\frac{1 \text{ min}}{60 \text{ s}}\right)\left(\frac{1 \text{hr}}{60 \text{min}}\right) = 11.6 \text{ hr}$$

$\boxed{\tau = 10 \text{ hrs}}$ (keeping the same number of significant figures as we were given)

More generally, for any L or W:

$$L = \sqrt{\frac{6094}{\text{aspect ratio}}}, \text{ where "aspect ratio"} = \frac{W}{L}$$

Therefore

$$\tau = \frac{\sqrt{\dfrac{\text{area}}{\text{aspect ratio}}}}{\text{wind velocity}}$$

For example, with an aspect ratio of 2, we would get τ = 8 hrs, which is not that different than what we found for the square.

(b) We want to find t, the time required for restoration of the air basin to a pristine state. We simply want to select any t, such that $t \gg \tau$. So, $\boxed{t = 1 \text{ day to } 1 \text{ week}}$ is sufficient. This assumes that the wind itself is pristine.

1.10

To find the characteristic time needed for the contaminant to return to its pre-spill level, we need to express the stock and flows in terms of known variables. Our system looks like:

So our stock is actually V, the lake volume, since the characteristic time required for flushing M from the lake is the same as the characteristic time required for flushing water from the lake.

Our flows can be written as either the inflow ($=F_i$) or the outflow ($=F_e+F_o$). We assume that the inflow equals the outflow.

Therefore, our characteristic time is:

$$\boxed{\tau = \frac{V}{F_i} = \frac{V}{F_e+F_o}}$$

1.11

Let's first find the number of democrats in the Senate after two years (i.e. one election). Of the 33.33 ($=\frac{1}{3}$ of the Senate) senators replaced or reelected, $\frac{2}{3}$, or 22.22, are democrats. Therefore the number of the democrats after the first election is:

$$\underbrace{50}_{\substack{\text{\# to}\\ \text{start}\\ \text{with}}} - \underbrace{16.665}_{\substack{\text{\# at end}\\ \text{of 6-year}\\ \text{term}}} + \underbrace{22.22}_{\substack{\text{\# put}\\ \text{into office}}} = 55.555 \text{ democrats}$$

This assumes that of the 33.33 senators who are at the end of their 6-year term, half are democrats.

$\boxed{1.11}$ (Continued)

Using the same assumption (that half of the seats put up for election were held by democrats) let's find the number of democrats after the second election

$$\underbrace{55.555}_{\substack{\text{\# to start}\\ \text{with}}} - \underbrace{16.665}_{\substack{\text{\# at end}\\ \text{of 6-yr}\\ \text{term}}} + \underbrace{22.22}_{\substack{\text{\# put into}\\ \text{office}}} = 61.11 \approx \boxed{61 \text{ democrats}}$$

$\boxed{1.12}$

Find the stock of water in the body first:

$$\text{STOCK} = (70 \text{ kg body})\left(0.9 \frac{\text{kg } H_2O}{\text{kg body}}\right) = \underline{63 \text{ kg}}$$

Now find the flows. Since the body's water content is constant over time, the inflow equals the outflow. The inflow is:

$$\text{FLOW} = \left(1500 \frac{g}{\text{day}} + 700 \frac{g}{\text{day}} + 300 \frac{g}{\text{day}}\right)\frac{1 \text{ kg}}{10^3 g} = 2.5 \frac{\text{kg}}{\text{day}}$$

The characteristic time is:

$$\tau = \frac{\text{STOCK}}{\text{FLOW}} = \frac{63 \text{ kg}}{2.5 \text{ kg/day}} = \boxed{25 \text{ days}} \approx 1 \text{ month}$$

$\boxed{1.13}$

We are given that the capacity of the Shasta reservoir is 4,552,000 acre-feet and that the average annual inflow is 5,439,000 acre-feet.

(a) The conversions are:

$$\text{CAPACITY}: (4{,}552{,}000 \text{ a-f})\left(43{,}560 \frac{ft^3}{\text{a-f}}\right)\left(\frac{1 m^3}{35.31 ft^3}\right) = \boxed{5.6 \times 10^9 m^3}$$

$$\text{INFLOW}: (5{,}439{,}000 \text{ a-f})\left(43{,}560 \frac{ft^3}{\text{a-f}}\right)\left(\frac{1 m^3}{35.31 ft^3}\right) = \boxed{6.7 \times 10^9 m^3 yr^{-1}}$$

$\boxed{1.13}$ (continued)

(b) The characteristic time of a water molecule is found by:

$$\tau = \frac{\text{STOCK}}{\text{FLOW}} = \frac{\text{CAPACITY}}{\text{INFLOW}} = \frac{5.6 \times 10^9\ m^3}{6.7 \times 10^9\ m^3/yr} = 0.836\ yr$$

$$\tau = (0.836\ yr)\left(365\ \frac{days}{yr}\right) = \boxed{305\ days}$$

(c) Because the chemical mixes thoroughly with the reservoir water and because it is inert, the characteristic time needed for the water to return to its pre-spill condition is the same as the characteristic time for a water molecule in the reservoir. Therefore:

$$\tau = \boxed{305\ days}$$

(d) The time is found by:

$$t = (5.6 \times 10^9\ m^3)\left(\frac{1\ \text{person-day}}{1400\ L}\right)\left(\frac{10^3 L}{m^3}\right)\left(\frac{1}{30 \times 10^6\ \text{persons}}\right)$$

$$\boxed{t = 133\ days}$$

(e) Use the concept of material balances to find how long it will take for the reservoir to go dry. Using a material balance on water:

$$\frac{\Delta S}{\Delta t} = f_{in} - f_{out}$$

where

$\Delta S/\Delta t$ = change in (water) stock with time
f_{in} = flow in
f_{out} = flow out

If the reservoir goes dry, then $\Delta S = -5.6 \times 10^9 m^3$. Since the reservoir level is currently unchanging, then $f_{in} = f_{out}$. If we reduce the inflow by 50%, then $f_{in} = \frac{1}{2} f_{out}$. Now we can solve for Δt:

$$\Delta t = \frac{\Delta S}{\frac{1}{2} f_{out} - f_{out}} = \frac{\Delta S}{-\frac{1}{2} f_{out}} = \frac{-5.6 \times 10^9 m^3}{-\frac{1}{2}\left(6.7 \times 10^9 \frac{m^3}{yr}\right)} = \boxed{1.7\ yrs}$$

$\approx$ 620 days

1.13 (continued)

(f) We can use the concept of material balances again to find the time required for the capacity of the reservoir to be depleted by 50%. Using a material balance on the silt:

$$\frac{\Delta S}{\Delta t} = f_{in} - f_{out}$$

where

ΔS = change in (silt) stock = $\frac{1}{2}(5.6 \times 10^9 \, m^3)$
(since we want to know when the silt will "take up" half the reservoir capacity)
Δt = unknown
f_{in} = flow of silt in = $0.0023 \left(6.7 \times 10^9 \frac{m^3}{yr}\right)$
$f_{out} = 0$

so

$$\Delta t = \frac{\Delta S}{f_{in} - f_{out}} = \frac{\frac{1}{2}(5.6 \times 10^9 \, m^3)}{0.0023 \left(6.7 \times 10^9 \frac{m^3}{yr}\right)} = \boxed{182 \text{ years}}$$

1.14

We are given that the mass fraction of sulfate (SO_4^{2-}) in seawater is 2.7 g kg^{-1}. (Note that there are 0.334 g S per g sulfate). We are also given the total mass of the oceans to be 1.4×10^{21} kg.

(a) The total mass is found by:

$$M_S = \left(2.7 \frac{g \, SO_4^{2-}}{kg \text{ seawater}}\right)\left(0.334 \frac{g \, S}{g \, SO_4^{2-}}\right)\left(1.4 \times 10^{21} \, kg \text{ seawater}\right)$$

$$M_S = \boxed{1.3 \times 10^{21} \, g} = 1.3 \times 10^{15} \text{ metric tonnes}$$

(b) The total inflow of sulfur into the oceans is:

$$\text{INFLOW} = 160 \times 10^{12} \frac{g}{yr} + 100 \times 10^{12} \frac{g}{yr} = 2.6 \times 10^{14} \frac{g}{yr}$$

Therefore the characteristic time of sulfur in the oceans is:

$$\tau = \frac{\text{STOCK}}{\text{FLOW}} = \left(\frac{1.3 \times 10^{21} \, g \, S}{2.6 \times 10^{14} \, g \, S/yr}\right) = \boxed{5 \times 10^6 \, yr}$$

$\boxed{1.15}$

(a) First, find the dimensions of an olympic-sized pool:

L: 50 m long
W: 8 lanes (9 ft each) + 2 washout lanes (1.5 ft each)
D: 2 to 3.5 m deep (take 2.7 m for average)

Therefore, the volume is:

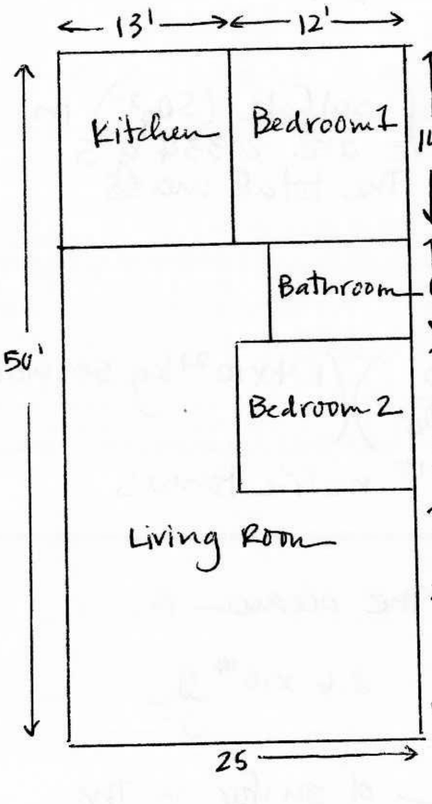
$$V = (50\text{ m})\left(\left\{8\text{ lanes} \times 9\text{ft} + 2\text{ lanes} \times 1.5\text{ ft}\right\} \times \frac{0.3048\text{ m}}{\text{ft}}\right)(2.7\text{ m})$$

$$V = 3086\text{ m}^3$$

Now, using the density of water (1 g cm^{-3}) and the molecular weight of water (18 g mol^{-1}); the total moles of water in the pool are:

$$\text{Moles} = 3086\text{ m}^3 \times \frac{10^6\text{ cm}^3}{\text{m}^3} \times \frac{1\text{ g}}{\text{cm}^3} \times \frac{1\text{ mole}}{18\text{ g}} \approx \boxed{2 \times 10^8\text{ moles}}$$

(b) We might expect a typical single family home to look like:



Assuming that the space occupied by furniture etc. is negligible:

$$\text{Volume} = 50' \times 25' \times 8' = 10{,}000\text{ ft}^3$$

$$V = (10{,}000\text{ ft}^3)\left(0.3048^3\ \frac{\text{m}^3}{\text{ft}^3}\right) = 283\text{ m}^3$$

Assuming $P = 1$ atm, $T = 293$ K:

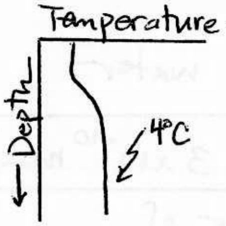
$$n = \frac{PV}{RT} = \frac{(1\text{ atm})(283\text{ m}^3)}{\left(82.05 \times 10^{-6}\ \frac{\text{atm m}^3}{\text{mol K}}\right)(293\text{ K})}$$

$$\boxed{n \approx 1 \times 10^4\text{ moles}}$$

Chapter 2

2.1

This density characteristic of water has important consequences for the temperature stratification of water bodies – most notably lakes – in cold-winter climates. When lake water cools the densest 4°C water will sink, leaving even cooler water at the surface (see temperature profile at left). The cool surface water can then freeze (and, indeed, ice is less dense than water). Thus instead of freezing from the bottom up, the lake freezes from the top – leaving fish and plankton with room to live.



2.2

(a) WATER:

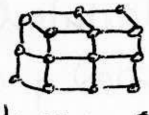
$$(1\ \mathrm{L\,H_2O})\left(10^3\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{g\,H_2O}}{\mathrm{mL\,H_2O}}\right)\left(\frac{1\ \mathrm{mol\,H_2O}}{18\ \mathrm{g}}\right) = \boxed{56\ \frac{\mathrm{mol\,H_2O}}{\mathrm{L}}}$$

AIR:

Using the Ideal Gas Law $\left(\frac{n}{V} = \frac{P}{RT}\right)$:

$$\frac{(1\ \mathrm{atm})}{\left(82.05\times10^{-3}\ \frac{\mathrm{L\cdot atm}}{\mathrm{mol\ K}}\right)(293\ \mathrm{K})} = \boxed{0.042\ \frac{\mathrm{mol\ air}}{\mathrm{L}}}$$

(b) We can assume the air molecules are in a cubic lattice:



The average volume occupied by a gas molecule is:

$$\left(\frac{1\ \mathrm{L\ air}}{0.042\ \mathrm{mol\ air}}\right)\left(\frac{1\ \mathrm{mol}}{6.02\times10^{23}\ \mathrm{molecules}}\right)\left(\frac{10^3\ \mathrm{cm^3}}{\mathrm{L}}\right)$$

$$= 4.0\times10^{-20}\ \mathrm{cm^3\ molecule^{-1}}$$

Therefore, the linear distance associated with one molecule is:

$$\sqrt[3]{4.0\times10^{-20}\ \mathrm{cm^3}} = \boxed{3.4\times10^{-7}\ \mathrm{cm} \doteq 3\times10^{-9}\ \mathrm{m}}$$

So, the average distance from the center of one gas molecule to the center of its neighbor is ~3 nm.

$\boxed{2.2}$ (continued)

(c) We can assume that the water molecules are in a cubic lattice. The average volume occupied by one water molecule is:

$$\left(\frac{1\ \text{L}\ H_2O}{56\ \text{mol}}\right)\left(\frac{1\ \text{mol}}{6.02\times10^{23}\ \text{molecules}}\right)\left(\frac{10^3\ \text{cm}^3}{\text{L}}\right)$$
$$= 3.0\times10^{-23}\ \text{cm}^3\ \text{molecule}^{-1}$$

The linear distance associated with one water molecule is:

$$\sqrt[3]{3.0\times10^{-23}\ \text{cm}^3} = \boxed{3.1\times10^{-8}\ \text{cm} \approx 3\times10^{-10}\ \text{m}}$$

So, the average distance from the center of one water molecule to the center of its neighboring water molecule is ~ 0.3 nm, which is approximately the size of a water molecule.

(d) From Figure 2A.1 the volume of the water in the oceans is $1400\times10^{15}\ \text{m}^3$. The total mass of water is:

$$(1400\times10^{15}\ \text{m}^3)\left(\frac{1000\ \text{kg}\ H_2O}{\text{m}^3}\right) = 1.4\times10^{21}\ \text{kg}\ H_2O$$

The mass of oxygen is:

$$(1.4\times10^{21}\ \text{kg}\ H_2O)\left(\frac{16\ \text{kg}\ O}{18\ \text{kg}\ H_2O}\right) = \boxed{1.2\times10^{20}\ \text{kg}\ O}$$

(e) From Table 2.B.1 the mole fraction of atmospheric species in dry air can be recalculated for air with 2% H_2O using:

$$Y_{i,\text{moist}} = Y_{i,\text{dry}}(1 - Y_{H_2O})$$

We get the following recalculated mole fractions:

SPECIES	MOLE FRACTION (DRY)	MOLE FRACTION (2% H_2O)
N_2	0.7808	0.7652
O_2	0.2095	0.2053
H_2O	0	0.02
Ar	0.0093	0.00911
CO_2	0.00035	0.000343

$\boxed{2.2}$ (continued)

(e) From this we can calculate the molecular weight of air with 2% water:

$$MW_{air} = \underbrace{\left(28\ \frac{g}{mol}\right)(0.7652)}_{N_2} + \underbrace{\left(32\ \frac{g}{mol}\right)(0.2053)}_{O_2} + \underbrace{\left(18\ \frac{g}{mol}\right)(0.02)}_{H_2O} + \underbrace{\left(40\ \frac{g}{mol}\right)(0.00911)}_{Ar} + \underbrace{\left(44\ \frac{g}{mol}\right)(0.000343)}_{CO_2}$$

$$MW_{air} = 28.73\ g\ mol^{-1}$$

Now we can use the following expression to get the mass fraction of each atmospheric species:

$$mole_{species} = \frac{(\text{mole fraction}_{species})(MW_{species})}{MW_{air}}$$

We get the following mass fractions:

SPECIES	MASS FRACTION
N_2	0.7456
O_2	0.2286
H_2O	0.0125
Ar	0.0127
CO_2	0.00053

Knowing that the total mass of the atmosphere is 5.1×10^{18} kg, we can calculate the mass of each element.

NITROGEN: All N is in N_2

$$Mass_N = (0.7456)(5.1 \times 10^{18}\ kg) = \boxed{3.8 \times 10^{18}\ kg}$$

OXYGEN: O is in H_2O, O_2, CO_2

$$Mass_O = \left[\left(\frac{16}{18}\right)(0.0125) + (0.2286) + \left(\frac{32}{44}\right)(0.00053)\right] \times (5.1 \times 10^{18}\ kg)$$

$$Mass_O = \boxed{1.2 \times 10^{18}\ kg}$$

$\boxed{2.2}$ (continued)

(e)

HYDROGEN: All H is in H_2O

$$\text{Mass}_H = \left(\frac{2}{18}\right)(0.0125)(5.1\times10^{18}\ kg) = \boxed{7.1\times10^{15}\ kg}$$

CARBON: All C is in CO_2

$$\text{Mass}_C = \left(\frac{12}{44}\right)(0.00053)(5.1\times10^{18}\ kg) = \boxed{7.4\times10^{14}\ kg}$$

$\boxed{2.3}$

(a) Using the ideal Gas Law:

$$\frac{n}{V} = \frac{P}{RT}, \text{ where } R = 82.05\times10^{-3}\ \frac{L\cdot atm}{mol\ K}$$

$$\text{and } \frac{n}{V} = \frac{1\ mol}{22.4\ L}$$

Therefore:

$$\frac{1\ mol}{22.4L} = \frac{P}{\left(82.05\times10^{-3}\ \frac{L\cdot atm}{mol\ K}\right)(T)}$$

So:

$$\frac{P}{T} = \frac{1}{273}\left[\frac{atm}{K}\right]$$

An obvious choice for P would be 1 atm, thus the temperature would be 273 K. So the conditions under which 1 mole of air occupies 22.4 L is:

$$\boxed{\begin{array}{l} P = 1\ atm \\ T = 273\ K = 0°C \end{array}}$$

(b) Using the Ideal Gas Law again:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(82.05\times10^{-3}\ \frac{L\cdot atm}{mol\ K}\right)(293\ K)}{1\ atm}$$

$$= \boxed{24\ \frac{L}{mol}\ \text{air}}$$

$\boxed{2.4}$

(a) We can find the number of molecules of water with the following expression:

$$\text{Molecules}_{H_2O} = (\text{Mass}_{\text{atmosphere}})(\text{MW}_{\text{air}})^{-1}(\text{mole fraction}_{H_2O})$$
$$\times (\text{Avogadro's number})$$

From problem 2.2 above we know:

$$\left.\begin{aligned} \text{Mass}_{\text{atmosphere}} &= 5.1 \times 10^{18}\ \text{kg} \\ \text{MW}_{\text{air}} &= 28.73\ \text{g mol}^{-1} \\ \text{Mole fraction}_{H_2O} &\approx 0.02 \end{aligned}\right\} \text{reasonable estimates}$$

Therefore, the number of water molecules is:

$$(5.1 \times 10^{18}\ \text{kg})\left(\frac{1\ \text{mol}}{28.73\ \text{g}}\right)\left(\frac{10^3\ \text{g}}{\text{kg}}\right)(0.02)\left(6.02 \times 10^{23}\ \frac{\text{molecules}}{\text{mol}}\right)$$
$$= \boxed{2.1 \times 10^{42}\ \text{molecules}}$$

(b) Recall that:

$$\tau = \text{residence time} = \frac{\text{stock}}{\text{flow}}$$

In this case, the stock is what we found in part (a): the total number of water molecules in the atmosphere. We can convert the stock into a volume of water:

$$(2.1 \times 10^{42}\ \text{molecules})\left(\frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{moloc}}\right)\left(\frac{18\ \text{g}}{\text{mol}}\right)\left(\frac{1\ \text{cm}^3}{\text{g}\ H_2O}\right)\left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right)$$
$$= 6.3 \times 10^{13}\ \text{m}^3\ H_2O$$

The flow to the Earth's surface, then, is:

$$\text{Flow} = \frac{\text{stock}}{\tau} = \frac{6.3 \times 10^{13}\ \text{m}^3}{(9\ \text{days})(86{,}400\ \frac{\text{s}}{\text{day}})}$$

$$\boxed{\text{Flow} = 8.1 \times 10^{7}\ \text{m}^3\ \text{s}^{-1}}$$

2.4 (continued)

(c) We first need to know the surface area of the Earth. Given that the mean radius of the Earth is 6370 km, the surface area is:

$$A_{Earth} = 4\pi r^2 = 4(3.1416)(6370\ km)^2\left(10^6\ \frac{m^2}{km^2}\right)$$

$$= 5.1 \times 10^{14}\ m^2$$

The average rainfall is found by:

$$\frac{\left(8.1 \times 10^7\ \frac{m^3}{s}\right)\left(86400\ \frac{s}{day}\right)\left(365\ \frac{days}{yr}\right)}{5.1 \times 10^{14}\ m^2}$$

$$\cong \boxed{5\ m\,yr^{-1} = 500\ cm\ yr^{-1}}$$

(d) Berkeley, California receives approximately 50 cm yr⁻¹ on average, and thus receives much less rainfall than the Earth's average. Las Vegas, Nevada, receives even less rainfall than Berkeley: 11 cm yr⁻¹. Compare both Berkeley and Las Vegas to Kukui, Maui, Hawaii, with 1878 cm yr⁻¹.

2.5

(a) We are given that T = 35°C (= 308 K), V = 1000 m³, P = 3 atm, and the composition of the gas is 65% CH_4 and 35% CO_2.

The mass of methane is:

$$Mass_{CH_4} = (Moles_{CH_4})(MW_{CH_4})$$

$$= \left(\frac{PV}{RT}\right)(MW_{CH_4})$$

$$= \frac{(0.65 \cdot 3\ atm)(1000\ m^3)}{\left(82.05 \times 10^{-6}\ \frac{m^3\ atm}{mol\ K}\right)(308\ K)}\left(16\ \frac{g}{mol}\right)\left(\frac{1\ kg}{10^3\ g}\right)$$

$$\boxed{Mass_{CH_4} = 1.2 \times 10^3\ kg}$$

The mass of carbon dioxide is:

$$Mass_{CO_2} = \frac{(0.35 \cdot 3\ atm)(1000\ m^3)}{\left(82.05 \times 10^{-6}\ \frac{m^3\ atm}{mol\ K}\right)(308\ K)}\left(44\ \frac{g}{mol}\right)\left(\frac{1\ kg}{10^3\ g}\right)$$

$$\boxed{Mass_{CO_2} = 1.8 \times 10^3\ kg}$$

$\boxed{2.5}$ (continued)

(b) Now $T = 25°C = 298\ K$.

The mass of methane is:

$$Mass_{CH_4} = \frac{(0.65 \cdot 3\ atm)(1000\ m^3)}{(82.05 \times 10^{-6}\ \frac{m^3\ atm}{mol\ K})(298\ K)} \left(16 \frac{g}{mol}\right)\left(\frac{1\ kg}{10\ g}\right)$$

$$Mass_{CH_4} = \boxed{1.3 \times 10^3\ kg}$$

The mass of carbon dioxide is:

$$Mass_{CO_2} = \frac{(0.35 \cdot 3\ atm)(1000\ m^3)}{(82.05 \times 10^{-6}\ \frac{m^3\ atm}{mol\ K})(298\ K)} \left(44 \frac{g}{mol}\right)\left(\frac{1\ kg}{10^3 g}\right)$$

$$Mass_{CO_2} = \boxed{1.9 \times 10^3\ kg}$$

(c) From part (b) we know that the stock of gas is:

$$STOCK = 1.3 \times 10^3\ kg + 1.9 \times 10^3\ kg = 3.2 \times 10^3\ kg$$

Therefore, the characteristic residence time of a gas molecule is:

$$\tau = \frac{STOCK}{FLOW} = \frac{3.2 \times 10^3\ kg}{400\ \frac{kg}{d}} = \boxed{8\ days}$$

$\boxed{2.6}$

Water in home AIR:

To find the number of moles of water we can use the Ideal Gas Law. But first we need to find the partial pressure of water, which we can do since we know the relative humidity.

$$RH = \frac{P_{H_2O}}{P^o_{H_2O}} \times 100 = \frac{\text{actual partial pressure of water}}{\text{saturation vapor pressure}}$$

From Figure 3.B.1 we see that $P^o_{H_2O}$ at 23°C (a reasonable home temperature) is approximately 2700 Pa. Therefore:

$$P_{H_2O} = 0.5\ (2700\ Pa)\left(\frac{1\ atm}{1.01325 \times 10^5\ Pa}\right) = 0.013\ atm$$

$\boxed{2.6}$ (continued)

Therefore, the number of moles of water is:

$$n = \frac{PV}{RT} = \frac{(0.013\ \text{atm})(300\,\text{m}^3)}{\left(82.05\times10^{-6}\ \frac{\text{atm m}^3}{\text{mol K}}\right)(296\ \text{K})} \cong 170\ \text{moles}$$

Water in glass:

$$n = (250\ \text{cm}^3)\left(\frac{1\,\text{g}\ H_2O}{\text{cm}^3\ H_2O}\right)\left(\frac{1\,\text{mol}\ H_2O}{18\,\text{g}}\right) = 14\ \text{moles}$$

So, there is more than 10 times as much water in the home air as in the glass.

$\boxed{2.7}$

(a) In dry air:

$$Y_{O_2} = 20.95\ \%$$

In air with 2% water vapor:

$$Y_{O_2} = 20.95\,\%\,(1-0.02) = \boxed{20.53\%}$$

(b) The molecular weight of air is found by:

$$MW_{air} = \sum_{\text{all } i} (MW_i)(Y_i),$$

where MW_i is the molecular weight of atmospheric species i, and Y_i is the mole fraction. The calculation is as follows:

SPECIES	MW_i [$\frac{g}{mol}$]	Y_i [–]	$(MW_i)(Y_i)$ [$\frac{g}{mol}$]
N_2	28	(0.7809)(1-0.02)	21.42
O_2	32	(0.2095)(1-0.02)	6.57
Ar	40	(0.0093)(1-0.02)	0.36
CO_2	44	(0.00035)(1-0.02)	0.02
H_2O	18	0.2	0.36
			$\sum_i = 28.74$

Therefore, the molecular weight of air with 2% water vapor is:

$$\boxed{MW_{air} = 28.7\ g\ mol^{-1}}$$

2.8

The diver is able to float because its mass (= test tube + air + water) is less than the mass of water it displaces. When the bottle is squeezed the pressure inside increases. The water is incompressible. As the air inside the diver is compressed, more water enters the diver thus increasing the total mass of the diver. If enough pressure is applied, the mass of the diver becomes greater than the mass of the water it displaces. The diver then sinks.

2.9

(a) Biochemical oxygen demand refers to the amount of oxygen required to oxidize decomposable compounds. These compounds are organic in nature, and include both soluble and nonsoluble constituents.

(b) Phosphate is a macronutrient for lake biota. Thus, an increase in phosphate inputs to a lake can increase algae growth, thus increasing the flux of dead algae to the lake sediments. The bacterial decomposition of these algae ~ which are a form of BOD ~ leads to the depletion of oxygen in the deep lake water. Low oxygen levels can be harmful to fish, and can also lead to the release of toxic compounds (ammonia, hydrogen sulfide) from the sediments.

(c) CO_2 and CH_4 are both greenhouse gases. Both compounds strongly absorb infrared radiation. Thus, infrared radiation emitted by the Earth's surface is increasingly "trapped" by CO_2, CH_4, and other greenhouse gases in the atmosphere. The radiation energy trapped or absorbed by these gases is translated into thermal energy, thus increasing the temperature of the atmosphere. This temperature increase ~ or global warming ~ may likely have profound impacts on global precipitation patterns, global sea levels, and other climate phenomena.

$\boxed{2.12}$

(a) Hardness is defined as the sum of the normalities of the multivalent cations. Recall that normality is defined as:

$$N = M \times |\text{Net charge}|,$$

where M = molarity (moles liter^{-1}). In this case, the three species that contribute the most to hardness (i.e. have the highest normalities) are also the 3 multivalent cation species with the highest molar concentrations:

① Ca^{2+}
② Mg^{2+}
③ Al^{3+}

(b) The total hardness is found by:

$$TH = \left[\underbrace{(245\times10^{-6})(2)}_{Ca^{2+}} + \underbrace{(74\times10^{-6})(2)}_{Mg^{2+}} + \underbrace{(3.7\times10^{-6})(3)}_{Al^{3+}}\right]\frac{eq}{L}$$

$$\boxed{\begin{aligned} TH &= 650\times10^{-6}\ eq\ L^{-1} \\ &= 0.65\ meq\ L^{-1}\end{aligned}}$$

(c) Recall that ionic strength is defined as:

$$I = \frac{1}{2}\sum_{\text{for all } i} c_i z_i^2$$

where c_i is the molar concentration of species i, and z_i is the net charge of the species. The five species for which $\frac{1}{2}c_i z_i^2$ is the highest are:

① Ca^{2+}
② HCO_3^-
③ Mg^{2+}
④ SO_4^{2-}
⑤ Na^+

(d) The total ionic strength caused by these five species is found by:

$$I = \frac{1}{2}\Big[(245\times10^{-6})(2)^2 + (570\times10^{-6})(1)^2 + (74\times10^{-6})(2)^2 + (72\times10^{-6})(2)^2 + (200\times10^{-6})(1)^2\Big]\ M$$

$$\boxed{\begin{aligned} I &= 1.2\times10^{-3}\ M \\ &= 1.2\ mM\end{aligned}}$$

$\boxed{2.13}$

Molarity and normality are calculated as follows:

$$\text{Molarity} = M = \left(\begin{matrix}\text{mass}\\ \text{concentration}\end{matrix}\right)\left(\frac{1}{\text{molecular weight}}\right)$$

$$\text{Normality} = N = M \times |\text{net charge}|$$

Using these definitions, we get the following results for Al^{3+}, Ba^{2+}, F^-, and NO_3^-:

Species	Mass concentration [mg L⁻¹]	MW [g mol⁻¹]	Charge [–]	M [mol L⁻¹]	N [eq L⁻¹]
Al^{3+}	0.19	27	+3	7.0×10^{-6}	2.1×10^{-5}
Ba^{2+}	0.16	134	+2	1.2×10^{-6}	2.3×10^{-6}
F^-	0.24	19	−1	1.3×10^{-5}	1.3×10^{-5}
NO_3^-	1.02	62	−1	1.6×10^{-5}	1.6×10^{-5}

$\boxed{2.14}$

(a) The principle of electroneutrality requires that $\sum_{\text{for all } i} z_i C_i = 0$. Let's consider anions and cations separately:

ANIONS

Species	Charge (= z) [–]	MW_i [g mol⁻¹]	C_i [mmol L⁻¹]	$z_i C_i$ [meq L⁻¹]
Cl^-	−1	35	0.231	−0.231
SO_4^{2-}	−2	96	0.066	−0.132
F^-	−1	19	0.021	−0.021
NO_3^-	−1	62	0.013	−0.013
HCO_3^-	−1	61	0.267	−0.267
OH^-	−1	17	0.001*	−0.001

$$\Longrightarrow \sum_{\text{anions}} z_i C_i = -0.665 \text{ meq L}^{-1}$$

* Note that C_{OH^-} was calculated as follows:

$$[OH^-] = \frac{K_{OW}}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6}\,M = 10^{-3}\,mM$$

$\boxed{2.14}$ (continued)

(a)

CATIONS

Species	Charge (= z) [–]	MW_i [g mol^{-1}]	C_i [mmol L^{-1}]	z_iC_i [meq L^{-1}]
Ca^{2+}	+2	40	0.168	+0.335
Na^{+}	+1	23	0.104	+0.104
Al^{3+}	+3	27	0.0037	+0.011
K^{+}	+1	39	0.0020	+0.002
Fe^{+}	+3	56	0.0011	+0.002
H^{+}	+1	1	0.00001	+0.00001

$$\Rightarrow \sum_{\text{cations}} z_iC_i = +0.454 \text{ meq L}^{-1}$$

$$\text{Therefore } \sum_{\text{for all } i} z_iC_i = -0.665 \frac{\text{meq}}{\text{L}} + 0.454 \frac{\text{meq}}{\text{L}} = -0.21 \frac{\text{meq}}{\text{L}}$$

This suggests that a significant ion is missing from the list, and it is a cation.

(b) Magnesium is one of the most abundant metals in the earth's crust, and often exists as Mg^{2+}. If Mg^{2+} were the missing cation, we would need the following mass concentration:

$$\left(0.21 \frac{\text{meq}}{\text{L}}\right)\left(\frac{1 \text{ mmol}}{2 \text{ meq}}\right)\left(24 \frac{\text{mg}}{\text{mmol}}\right) = 2.55 \text{ mg L}^{-1}\, Mg^{2+}$$

Let's see if we are missing this much TDS. The total TDS measured is 43.7 mg L^{-1}. The TDS of the reported species is:

$$\begin{aligned} TDS_{\text{reported}} &= (8.1 + 6.3 + 0.4 + 0.8 + 16.3 + 6.7 + 2.4 \\ &\quad + 0.1 + 0.08 + 0.06) \text{ mg L}^{-1} \\ &= 41.2 \text{ mg L}^{-1} \end{aligned}$$

So, it looks like we are indeed missing 43.7 − 41.2 = 2.5 mg L^{-1} of TDS, and $\boxed{Mg^{2+}}$ seems like a good guess.

$\boxed{2.15}$

(a) Total hardness is defined as the sum of the normalities of multivalent cations. The multivalent cations present in the river water are Ca^{2+} and Mg^{2+}. The hardness is calculated s follows:

Species	Mass Concentration [mg L^{-1}]	MW_i [g mol^{-1}]	M_i [mol L^{-1}]	N_i [eq L^{-1}]
Ca^{2+}	15	40	3.75×10^{-4}	7.5×10^{-4}
Mg^{2+}	4.1	24	1.71×10^{-4}	3.42×10^{-4}

$$\Sigma = 1.1 \times 10^{-3}$$

Therefore the total hardness is:

$$\boxed{TH = 1.1 \text{ meq } L^{-1}}$$

(b) Carbonate hardness (CH) is found by summing the normalities of CO_3^{2-} and HCO_3^-. If this sum is less than TH, then CH is set equal to this sum. If this sum is greater than TH, then CH = TH. In this case, the normalities of the carbonate species are as follows:

$$\overbrace{\left(0.0085\ \frac{mg}{L}\right)\left(\frac{1\,mmol}{60\,mg}\right)(2)}^{N_{CO_3^{2-}}} + \overbrace{\left(58.4\ \frac{mg}{L}\right)\left(\frac{1\,mmol}{61\,mg}\right)(1)}^{N_{HCO_3^-}}$$

$$= 0.96 \text{ meq } L^{-1}$$

Since this value is less than TH, $\boxed{CH = 0.96 \text{ meq } L^{-1}}$.

(c) We can assume that none of the components listed are filterable (although SiO_2 may be in the form of filterable particles, this is neglected here). Thus, TDS is found by:

$$TDS = \left[15 + 4.1 + 6.3 + 2.3 + 0.67 + 0.32 \times 10^{-3} + 58.4 + 0.0085 + 11.2 + 7.8 + 1 + 13.1\right] \text{mg } L^{-1}$$

$$\boxed{TDS = 120 \text{ mg } L^{-1}}$$

$\boxed{2.15}$ (continued)

(d) Alkalinity is defined as:

$$ALK = \left\{[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]\right\} \text{ eq } L^{-1}$$

In this case:

$$[H^+] = \left(0.32 \frac{\mu g}{L}\right)\left(\frac{1 g}{10^6 \mu g}\right)\left(\frac{1 \text{ mole}}{1 g}\right) = 3.2 \times 10^{-7} M$$

$$[OH^-] = \frac{10^{-14} M^2}{[H^+]} = \frac{10^{-14} M^2}{3.2 \times 10^{-7} M} = 3.13 \times 10^{-8} M$$

$$[HCO_3^-] = \left(58.4 \frac{mg}{L}\right)\left(\frac{1 g}{10^3 mg}\right)\left(\frac{1 mol}{61 g}\right) = 9.57 \times 10^{-4} M$$

$$[CO_3^{2-}] = \left(0.0085 \frac{mg}{L}\right)\left(\frac{1 g}{10^3 mg}\right)\left(\frac{1 mol}{60 g}\right) = 1.42 \times 10^{-7} M$$

Thus:

$$ALK = \left[3.13 \times 10^{-8} + 9.57 \times 10^{-4} + 1.42 \times 10^{-7} - 3.2 \times 10^{-7}\right] \frac{eq}{L}$$

$$\boxed{ALK = 0.96 \text{ meq } L^{-1}}$$

(e) Ionic strength is defined as:

$$I = \frac{1}{2} \sum_{\text{for all } i} C_i Z_i^2$$

where C_i is the molar concentration of species i, and Z_i is the net charge of species i. The ionic strength is calculated as follows:

SPECIES	MASS CONC. [mg L^{-1}]	MW_i [g mol^{-1}]	C_i [M]	Z_i [-]	$C_i Z_i^2$ [M]
Ca^{2+}	15	40	3.75×10^{-4}	+2	1.5×10^{-3}
Mg^{2+}	4.1	24	1.71×10^{-4}	+2	6.84×10^{-4}
Na^+	6.3	23	2.74×10^{-4}	+1	2.74×10^{-4}
K^+	2.3	39	5.90×10^{-5}	+1	5.90×10^{-5}
Fe^{3+}	0.67	56	1.20×10^{-5}	+3	2.44×10^{-4}
HCO_3^-	58.4	61	9.57×10^{-4}	−1	9.57×10^{-4}
CO_3^{2-}	0.0085	60	1.42×10^{-7}	−2	5.68×10^{-7}
SO_4^{2-}	11.2	96	1.17×10^{-4}	−2	4.68×10^{-4}
Cl	7.8	35.5	2.20×10^{-4}	−1	2.20×10^{-4}
NO_3^-	1	62	1.61×10^{-5}	−1	1.61×10^{-5}

$$\Rightarrow \boxed{I = 2.0 \times 10^{-3} M}$$

$\boxed{2.15}$ (continued)

(f) pH is defined as:

$$pH = -\log_{10}(\text{molar concentration of } H^+)$$

From part (d) we know $[H^+] = 3.2 \times 10^{-7}$ M.
Therefore:

$$\boxed{pH = -\log[3.2 \times 10^{-7}] = 6.5}$$

(g) The following condition must be met for the electroneutrality principle to be satisfied:

$$\underbrace{\sum c_i|z_i|}_{\text{for all anions}} = \underbrace{\sum c_i|z_i|}_{\text{for all cations}}$$

We can use the values calculated in part (e) for c_i and z_i.

For anions:

$$\sum c_i z_i = \{(9.57 \times 10^{-4})(1) + (1.42 \times 10^{-7})(2) + (1.17 \times 10^{-4})(2) + (2.20 \times 10^{-4})(1) + (1.61 \times 10^{-5})(1)\}\ M$$

$$= 1.43 \times 10^{-3}\ M$$

For cations:

$$\sum c_i z_i = \{(3.75 \times 10^{-4})(2) + (1.71 \times 10^{-4})(2) + (2.74 \times 10^{-4})(1) + (5.90 \times 10^{-5})(1) + (1.20 \times 10^{-5})(3)\}\ M$$

$$= 1.46 \times 10^{-3}\ M$$

Therefore, we have satisfied electroneutrality to within < 1%.

2.16

(a) ALUMINUM

Sources: Aluminum (Al) is the most abundant metal in the Earth's crust, and the third most abundant element overall. Thus, it enters drinking water through contact with soil media. Al is also added to drinking water as alum, which is a flocculant.

Adverse effects: Al inhibits brain enzymes, thus causing general neurological problems. Elevated levels of Al are found in the brain tissue of those suffering from Alzheimer's disease and dialysis encephalopathy syndrome. Al can substitute into calcium hydroxyapatite in bone and alter the form and function of bone.

(b) BARIUM

Sources: Barium (Ba) exists in nature as ores. Oil drilling operations, as well as copper smelting operations, use Ba and can both be potential sources for groundwater contamination. Ba is also found in bleach, dyes, ceramics, and glass.

Adverse effects: Ba causes gastrointestinal disturbances, muscular weakness, and high blood pressure.

(c) NITRATE

Sources: Nitrate (NO_3^-) most commonly enters surface water and groundwater from agricultural runoff, since it is an important component of fertilizer. NO_3^- is also present in livestock manure, and thus can come from stockyard runoff as well.

Adverse effects: In infants, NO_3^- causes methemoglobinemia. NO_3^- is reduced to nitrite (NO_2^-) in the intestine, and NO_2^- interferes with the oxygen carrying capacity of the blood.

$\boxed{2.16}$ (continued)

(d) ARSENIC

Sources: Arsenic (As) exists in nature as ores, and thus groundwater in contact with As-bearing deposits can become contaminated. Arsenic can also be found in agricultural runoff, where it is used as an herbicide.

Adverse effects: At low levels, As causes skin cancer and will harm developing fetuses. At high levels, As is lethal since it breaks down protein compounds in vein walls and causes a loss of fluid and blood circulation.

SOURCES OF INFORMATION:

① Fact Sheets from EPA office of Groundwater and Drinking Water.
② Fact Sheets from California EPA office of Environmental Health Hazard Assessment.

$\boxed{2.17}$

(a) Total hardness is defined as the sum of the normalities of multivalent cations in the water of interest.

(b) Calcium (Ca^{2+}) and magnesium (Mg^{2+}) are the two most important species that contribute to hardness in treated public water.

(c) $$TH = \{\underbrace{(0.3\times10^{-3}M)(2)}_{N_{Ca^{2+}}} + \underbrace{(0.1\times10^{-3}M)(2)}_{N_{Mg^{2+}}}\}\ \text{eq L}^{-1}$$

$$\boxed{TH = 8.0\times10^{-4}\ \text{eq L}^{-1} = 0.8\ \text{meq L}^{-1}}$$

$\boxed{2.17}$ (continued)

(d) The following table is helpful for our calculations:

SPECIES	MASS CONC [$mg\,L^{-1}$]	MW [$g\,mol^{-1}$]	M [$mol\,L^{-1}$]	N [$eq\,L^{-1}$]
Na^+	56	23	2.43×10^{-3}	2.43×10^{-3}
Ca^{2+}	40	40	1.00×10^{-3}	2.00×10^{-3}
Mg^{2+}	30	24	1.25×10^{-3}	2.50×10^{-3}
HCO_3^-	190	61	3.11×10^{-3}	3.11×10^{-3}
Cl^-	165	35.5	4.65×10^{-3}	4.65×10^{-3}
Al^{3+}	30	27	1.11×10^{-3}	3.33×10^{-3}

Therefore:

$$TH = \underbrace{2.00 \times 10^{-3} \frac{eq}{L}}_{Ca^{2+}} + \underbrace{2.50 \times 10^{-3} \frac{eq}{L}}_{Mg^{2+}} + \underbrace{3.33 \times 10^{-3} \frac{eq}{L}}_{Al^{3+}}$$

$TH = 7.8\ meq\ L^{-1}$

$CH = 3.1\ meq\ L^{-1}$

$NCH = TH - CH = 4.7\ meq\ L^{-1}$

Note: Although CO_3^{2-} is likely present, its concentration is going to be very small relative to HCO_3^- and thus will not contribute significantly to CH.

(e) We can use the table from part (d) to check the electroneutrality balance.

For anions: $\sum_i C_i z_i = \sum_i \text{Normalities}$

$$= \{3.11 \times 10^{-3} + 4.65 \times 10^{-3}\} \frac{eq}{L}$$

$$= 7.76\ meq\ L^{-1}$$

For cations: $\sum_i C_i z_i = \sum_i \text{Normalities}$

$$= 10.3\ meq\ L^{-1}$$

Thus, we are missing some anions, perhaps SO_4^{2-} or NO_3^-, and electroneutrality is <u>not</u> satisfied.

2.18

(a) Carbonate species, including HCO_3^- and CO_3^{2-}, are the dominant contributors to alkalinity in natural waters.

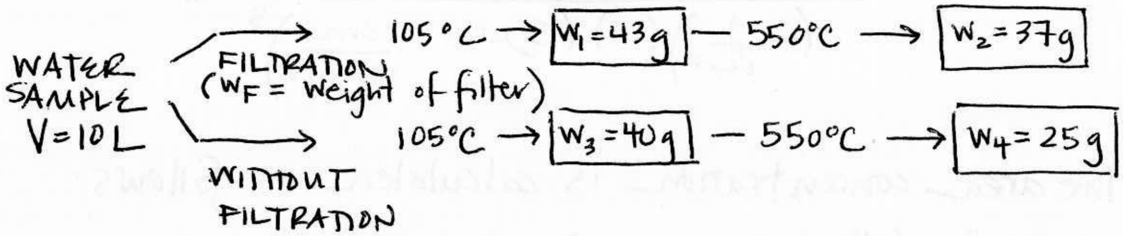
(b) Alkalinity is a measure of the capacity of a water to neutralize strong acid. Thus, a water with high alkalinity is capable of resisting pH changes. A water with high alkalinity may also have high carbonate hardness which can lead to the problems of scale in pipes, and "soap curd" formation during home cleaning activities.

(c) Any species that is capable of "taking up" a H^+ will contribute positively to alkalinity. These include:

CO_3^{2-}, PO_4^{3-}, HCO_3^-, OH^-, and HS^-

2.19

The following schematic will help us in our solids calculations.



$\underline{\underline{TS}}$ = total solids = $\frac{W_3}{V} = \frac{40\,g}{10\,L} = \underline{\underline{4\ g\ L^{-1}}}$

$\underline{\underline{TVS}}$ = total volative solids = $\frac{W_3 - W_4}{V} = \frac{(40-25)g}{10\,L} = \underline{\underline{1.5\ g\,L^{-1}}}$

$\underline{\underline{SS}}$ = suspended solids = $\frac{W_1 - W_F}{V} = \frac{(43-15)g}{10\,L} = \underline{\underline{2.8\ g\ L^{-1}}}$

$\underline{\underline{VSS}}$ = volatile suspended solids = $\frac{W_1 - W_2}{V} = \frac{(43-37)g}{10\,L}$
$= \underline{\underline{0.6\ g\ L^{-1}}}$

$\underline{\underline{TDS}}$ = $TS - SS = \underline{\underline{1.2\ g\ L^{-1}}}$

$\boxed{2.20}$

(a) The number concentration is calculated as follows:

$$\frac{\#}{cm^3} = \left(\frac{\text{mass particle}}{\text{volume } H_2O}\right)\left(\frac{\text{volume particle}}{\text{mass particle}}\right)\left(\frac{1 \text{ particle}}{\text{volume 1 particle}}\right)$$

$$\frac{\#}{cm^3} = (C)\left(\frac{1}{\rho}\right)\left(\frac{1}{\frac{\pi}{6} d_p^3}\right) = \frac{6C}{\rho \pi d_p^3}$$

where C = mass concentration
ρ = particle density
d_p = particle diameter

For sample A:

$$\frac{\#}{cm^3} = \frac{(6)\left(5 \frac{mg}{L}\right)\left(\frac{1000 L}{m^3}\right)\left(\frac{1 m^3}{10^6 cm^3}\right)\left(\frac{1 g}{1000 mg}\right)}{\left(2 \frac{g}{cm^3}\right)(\pi)\left(5 \mu m \cdot \frac{1 cm}{10^4 \mu m}\right)^3} = 3.8 \times 10^4$$

For sample B:

$$\frac{\#}{cm^3} = \frac{(6)\left(5 \frac{mg}{L}\right)\left(\frac{1000 L}{m^3}\right)\left(\frac{1 m^3}{10^6 cm^3}\right)\left(\frac{1 g}{1000 mg}\right)}{\left(2 \frac{g}{cm^3}\right)(\pi)\left(15 \mu m \cdot \frac{1 cm}{10^4 \mu m}\right)^3} = 1.4 \times 10^3$$

The area concentration is calculated as follows:

$$\frac{\mu m^2}{cm^3} = \left(\frac{\#}{cm^3}\right)\left(\frac{\text{cross-sectional area}}{\text{particle}}\right)$$

$$\frac{\mu m^2}{cm^3} = \frac{\#}{cm^3} \cdot \pi \left(\frac{d_p}{2}\right)^2$$

For sample A:

$$\frac{\mu m^2}{cm^3} = \left(3.8 \times 10^4 \frac{\#}{cm^3}\right)(\pi)\left(\frac{5 \mu m}{2}\right)^2 = 7.5 \times 10^5 \frac{\mu m^2}{cm^3}$$

$\boxed{2.20}$ (continued)

(a)

For Sample B:

$$\frac{\mu m^2}{cm^3} = \left(1.41 \times 10^3 \frac{\#}{cm^3}\right)(\pi)\left(\frac{15\ \mu m}{2}\right)^2 = 2.5 \times 10^5 \frac{\mu m^2}{cm^3}$$

Therefore our table looks like this:

	Sample A	Sample B
Concentration (#/cm^3)	3.8×10^4	1.4×10^3
Area Concentration ($\mu m^2/cm^3$)	7.5×10^5	2.5×10^5

(b)

$$\frac{\text{Turbidity A}}{\text{Turbidity B}} = \frac{7.5 \times 10^5\ \mu m^2\ cm^{-3}}{2.5 \times 10^5\ \mu m^2\ cm^{-3}} = 3$$

Therefore sample A is $\boxed{\text{3 times}}$ more turbid than sample B.

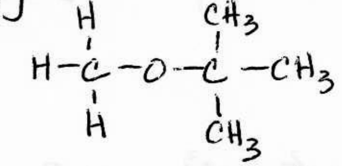
(c) A nephelometer is an instrument used to measure turbidity in a water sample. Unlike a photometer, which measures how much light is transmitted through a sample, a nephelometer measures how much light is scattered by a sample.

$\boxed{2.21}$

(a) MTBE is used as an oxygenated additive in gasoline. In 1988, USEPA approved the use of MTBE in gasoline up to 15% by volume. Currently, MTBE is added to about 30% of the gasoline consumed in the US and to virtually all of the gasoline consumed in CA.

(b) The extra oxygen atom in MTBE leads to more complete gasoline combustion and therefore a reduction in CO emissions. MTBE also helps to reduce SO_2 and VOC emissions by diluting the sulfur, aromatic, and olefinic contents of gasoline.

(c) The oxygen in MTBE provides better fuel combustion:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

(d) The majority of health risks associated with MTBE are due to airborne exposure. The current average ambient concentration in California is ~ 2 ppb. To receive an equivalent exposure from MTBE-contaminated drinking water, it would have to have ~ 70 ppb MTBE. Most data collected to date suggests that drinking water levels of MTBE are very low. Nevertheless, MTBE contamination of surface water and groundwater sources is attracting more attention. MTBE surface water contamination is a result of the use of gasoline-powered vehicles on lakes and rivers. Groundwater contamination is due to leaking underground storage tanks.

(e) Animal studies suggest that MTBE may be a weak carcinogen. The US EPA has suggested that MTBE should be considered as having a "human carcinogenic hazard potential."

$\boxed{2.21}$ (continued)

(f) The taste and odor thresholds are low for MTBE. Thus, water with low levels of MTBE tastes and smells like turpentine. Also, ecological effects from MTBE contamination of lakes, reservoirs, and rivers are possible, but not well-understood.

Chapter 3

3.1

(a) When a system is at chemical equilibrium, the concentrations of species in the system remain constant and the distribution of those species is determined by thermodynamics. A system that is not at equilibrium will tend to approach equilibrium at some rate. This rate is governed by chemical kinetics. Let's take the example of a system with 4 chemical species - A, B, C and D - which react according to the following expression:

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

Both k_f and k_b are rate constants which tell us how fast the reactions between A and B and between C and D respectively, proceed. The overall rate of the forward reaction is desribed by:

$$R_f = k_f[A][B]$$

Likewise, the overall rate of the backward reaction is:

$$R_b = k_b[C][D]$$

At equilibrium the rate of the forward reaction equals the rate of the backward reaction:

$$k_f[A][B] = k_b[C][D]$$

Rearranging, and recalling that an equilibrium constant is defined as the quotient of reaction products over reactants:

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = K_{eq}$$

Thus the equilibrium constant is a ratio of the kinetic rate constants, and equilibrium and kinetics are related.