

## Chapter 2: Analyzing Sustainability Using Engineering Science

2-1. Define the following terms or concepts:

**Answer:**

- a. **Law of electroneutrality**- states that the sum of all positive ions (cations) in solution must equal the sum of all the negative ions (anions) in solution, so that the net charge of all natural waters is equal to zero:  $\sum \text{cations} - \sum \text{anions} = 0$
- b. **Normality**- of a solution is the number of equivalents per liter, and can be determined by multiplying the concentration of a specie,  $MW_i$ , by the number of equivalents,  $z_i$ :  $N_i [eq/L] = (C_i [mol/L]) (z_i [equivalents/mol])$
- c. **Equivalent**- means that the number of charge equivalents (eq) associated with a compound is equal to the absolute value of the charge associated with the form of the dissolved ion. (example: the dissolved sodium ion,  $Na^+$ , has a charge of +1 or 1 equivalent)
- d. **Total Dissolved Solids (TDS)**- consist of salts and minerals that have been dissolved through natural weathering of soils or through the anthropogenic process
- e. **Total Suspended Solids (TSS)** - the materials that are floating or suspended in the water
- f. **Volatile Suspended Solids (VSS)** - determined by the weight of any particles that have evaporated from a filter after the filter is heated to 550°C
- g. **Fixed Solids** - determined by the weight of any particles remaining on a filter heated to 550°C
- h. **Total Hardness** - the sum of the concentration of the divalent cations (species with a charge of 2+) in water
- i. **Carbonate Hardness** - represents the portion of the diprotic ions that can combine with carbonates to form scaling
- j. **Noncarbonated Hardness** - the difference between total hardness and carbonate hardness
- k. **Chemical Reactivity** - the chemical's overall tendency to participate in a reaction

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- l. **Chemical Activity** - a standardized measure of chemical reactivity within a defined system
- m. **Standard State Activity** - Reference state of chemical reactivity
- n. **Activity Coefficient** - used to relate the standard chemical activity and the conditional chemical reactivity
- o. **Solubility** - the amount of a substance that can be dissolved into solution by a solvent
- p. **Precipitate** – The resulting solid form of a substance that forms from oversaturated concentrations in solution
- q. **Reduction–Oxidation Process** - occur when the oxidation state of participating atoms change
- r. **Ionic Reaction** - there is a change in ion–ion interactions and relationships
- s. **Dissolution Salts** - the process of a substance dissolving in solution
- t. **Sorbent** - the material into or onto which the sorbate is transferred
- u. **Sorbate** - the substance that is transferred from one phase to another

**2-2.** Mass and energy balances are helpful to track chemicals as they move from one **repository** to another, however, we must study the application as and principles of chemistry more closely to appreciate how these chemicals are transformed in the environment and also transform the earth's environment.

**2-3.** How much have carbon dioxide levels in the atmosphere have increased since the start of the industrial revolution?

**Answer:**

Carbon dioxide levels have increased by more than 30% since the industrial revolution.

**2-4.** What 5 elements are found in life on the planet?

**Answer:**

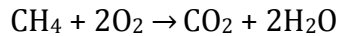
- Carbon
- Nitrogen
- Oxygen

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- Phosphorus
- Hydrogen

2-5. Write the balanced equation for the combustion of methane (CH<sub>4</sub>), in the presence of oxygen.

**Answer:**



2-6. How many atoms are in a mole?

**Answer**

$$1 \text{ mole} = 6.02 \times 10^{23} \text{ atoms}$$

2-7. What is the numerical value of  $R$  in [J/mol-K] in the ideal gas law?

**Answer:**

$$R = 8.314 \text{ [J/mol-K]}$$

2-8. Define the **Partial Pressure** of a gas.

**Answer:**

Partial Pressure is the pressure of each part of a gas that it exerts upon its surroundings.

2-9. What is the relationship between the concentration of a gas in air in mg/m<sup>3</sup> and ppm<sub>v</sub> at standard temperature and pressure?

**Answer:**

$$C_i \text{ [mg/m}^3\text{]} = \frac{C_i \text{ [ppmv]} MW_i}{24.5}$$

2-10. What is the relationship between the concentration of a gas in air in mg/m<sup>3</sup> and ppm<sub>v</sub> at non-standard temperature and pressure?

**Answer:**

$$C_i \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = \text{ppmv} \times MW_i \times \frac{1,000P}{RT}$$

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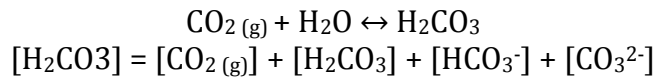
2-11. Relate Parts Per Billion (ppb<sub>v</sub>) to ppm<sub>v</sub>.

**Answer:**

$$1 \text{ ppm}_v = 1000 \text{ ppb}_v$$

2-12. Describe using chemical equations the forms of dissolved carbon dioxide in aqueous solution.

**Answer:**



2-13. The Normality of a solution is the number of equivalents per liter, and can be determined by multiplying the concentration of a specie, MW<sub>i</sub>, by the number of equivalents, z<sub>i</sub>.

**Answer:**

$$NB_i[\text{eq}/L] = (C_i [\text{mol}/L]) (z_i [\text{equivalents}/\text{mol}])$$

2-14. The concept of an equivalent weight, EW, may also be useful in calculations involving aqueous solutions. The Equivalent Weight of any specie, EW<sub>i</sub>, is equal to the molar mass divided by the number of equivalents associated with the dissolved ion.

**Answer:**

$$EW_i [\text{g}/\text{eq}] = \frac{MW_i [\text{g}/\text{mol}]}{z_i [\text{eq}/\text{mol}]}$$

2-15. The ionic strength, I, of a solution is the estimate of the overall concentration of dissolved ions in solution is defined by what?

**Answer:**

$$I = \frac{1}{2} \sum \text{all ions } C_i z_i^2$$

I = ionic strength [mol/L]

C<sub>i</sub> = concentration of each individual ion [mol/L]

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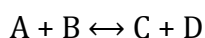
$Z_i$  = charge associated with each ion specie,  $i$

**2-16.** The activity coefficient is defined as the ratio of the reactivity per molecule of mol of A in a real system compared to the reactivity of A in the standard reference state.

**Answer:**

$$\gamma_A = \frac{\text{real reactivity per mole of A}}{\text{standard activity per mol of A}} = \frac{\{A\}}{[A]}$$

**2-17.** The fundamental parameter for equilibrium base models is the equilibrium constant,  $k$ .



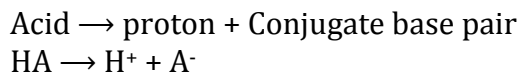
$$k_{\text{equilibrium}} = \frac{\{\text{products}\}}{\{\text{reactants}\}} = \frac{\{C\}\{D\}}{\{A\}\{B\}}$$

**2-18.** The pH of natural waters is important to biodiversity since most species are only tolerant of natural waters in the pH range from **6.5 to 8.5**.

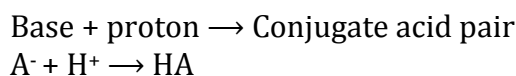
**2-19.** Phosphoric acid has the form  $H_3PO_4$ . List all the acids that may donate a hydrogen ion and the conjugate bases that may accept the proton for this acid compound.

**Answer:**

The acid that donates the hydrogen ion and the base that accepts the ion are collectively known as an acid conjugate base pair, as shown below:



OR



**2-20.** What is the primary characteristic of an amphoteric compound?

**Answer:**

It has substances that can either donate or receive a proton.

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2-21. Define the equilibrium constant for pure water.

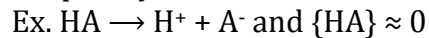
**Answer:**

$$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$$
$$K_w = \frac{\{H^+\}\{OH^-\}}{\{HOH\}} = \{H^+\}\{OH^-\} = 10^{-14}$$

2-22. What are the primary characteristics of a strong acid?

**Answer:**

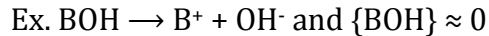
Strong acids completely dissociates when added to water



2-23. What are the primary characteristics of a strong base?

**Answer:**

Strong bases may be assumed to completely dissociate with a large value of  $k_b$ .



2-24. Write the equation that defines pH.

**Answer:**

$$\text{pH} = -\log\{\text{H}^+\}$$

2-25. Write the equation that defines pOH.

**Answer:**

$$\text{pOH} = -\log\{\text{OH}^-\}$$

2-26. Write the equation that relates  $k_w$ , pH, and pOH.

**Answer:**

$$K_w = \{H^+\}\{OH^-\} = 10^{-14}$$

2-27. What are the steps involved in modeling the effects of acids or bases in the natural environment?

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**Answer:**

- Step 1: Define the system boundaries.
- Step 2: Identify all the chemical species of interest.
- Step 3: Write the constraining chemical equations for the system, including equilibrium equations, the electroneutrality equation and mass balance equations.
- Step 4: Make any simplifying assumptions that are possible.
- Step 5: Algebraically solve the remaining independent equations and check the assumptions made to aid in solving the equations.

**2-28.** Define the primary characteristic of a weak acid that only partially dissociates in an aqueous solution is called a weak acid.

**Answer:**

Weak acids have small equilibrium constant ( $k_a$ ) values.

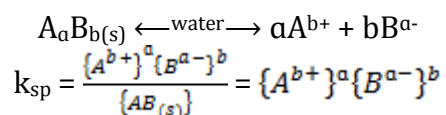
**2-29.** Define the primary characteristic of a weak acid that only partially dissociates in an aqueous solution is called a weak base.

**Answer:**

Weak bases have small equilibrium constant ( $k_b$ ) values.

**2-30.** The solubility-product constant, or solid-liquid equilibrium constant, is defined by what general reaction?

**Answer:**



**2-31.** What is the fraction of the total amount of A at equilibrium in the generic x-phase?

**Answer:**

$$f_{Ax} = \frac{\text{mass of A in phase } x}{\text{total mass of A}} = \frac{(C_{Ax})(V_x)}{(C_{Ax})(V_x) + (C_{Ay})(V_y)} = \frac{1}{1 + \frac{(C_A)(V_y)}{(C_{Ax})(V_x)}}$$

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2-32. The Freundlich isotherm is used to estimate the partitioning of pollutants from a more mobile phase in gas or water to the solid activated carbon material. The Freundlich equation has what form?

**Answer:**

$$q = KC^{1/n}$$

q = mass of sorbate sorbed per unit mass of sorbent (mg/g)

K = the Freundlich parameter that describes the partitioning  $\left(\frac{\text{mg/g}}{(\text{mg/L})^{1/n}}\right)$

C = the equilibrium sorbate concentration in the aqueous solution (mg/L)

n = Freundlich isotherm intensity parameter (unitless)

2-33. The octanol/water partition coefficient,  $K_{ow}$ , is defined by \_\_\_\_\_

**Answer:**

$$K_{ow} = \frac{\text{mg chemical/L octanol}}{\text{mg chemical/L water}}$$

2-34. The organic carbon normalized partition coefficient is defined as \_\_\_\_\_

**Answer:**

$$K_{oc} = \frac{\text{mg chemical/kg organic carbon}}{\text{mg chemical/L water}}$$

2-35. A 12 ounce can of soda contains about 40 grams of sugar. What is the concentration of sugar in a can of soda in mg/L?

**Answer:**

$$\frac{40\text{g sugar}}{12\text{oz soda}} \times \frac{1\text{oz}}{30\text{mL}} \times \frac{1000\text{mg}}{\text{g}} \times \frac{1000\text{mL}}{\text{L}} = 111,000 \frac{\text{mg}}{\text{L}}$$



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**2-36.** A 2 ounce shot of espresso serving contains 100 mg of caffeine. Professor Coffy often has a 16 ounce iced latte with 3 shots of espresso latte before his 8 am class.

a. What is the concentration of caffeine in mg/L in a single shot of espresso?

**Answer:**

$$1670 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ ppm}_m}{1 \frac{\text{mg}}{\text{L}_{(aq)}}} = 1670 \text{ ppm}_m$$

b. What is the concentration of caffeine in ppm in a single shot of espresso?

**Answer:**

$$\frac{3 \times 100 \text{ mg}}{16 \text{ oz}} \times \frac{1 \text{ oz}}{30 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 625 \frac{\text{mg}}{\text{L}} = 625 \text{ ppm}_m$$

c. What is the concentration of caffeine in his coffee drink?

**Answer:**

$$\frac{100 \text{ mg}}{2 \text{ oz}} \times \frac{1 \text{ oz}}{30 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 1670 \frac{\text{mg}}{\text{L}}$$

**2-37.** There is about 5 mg of caffeine in each shot of decaf espresso. The barista is being paid under the table by Mrs. Coffy to change the espresso shots to decaffeinated espresso in Professor Coffy's 16 ounce latte drink cup from problem 2.36.

a. How much caffeine in mg/L does Dr. Coffy consume if he drinks decaffeinated lattes before class?

**Answer:**

$$\frac{5 \times 3 \text{ mg}}{16 \text{ oz}} \times \frac{1 \text{ oz}}{30 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 31.25 \frac{\text{mg}}{\text{L}}$$

b. How many 16 oz decaf lattes must he drink before he consumes the amount of caffeine equivalent to his old 3 shots of caffeinated espresso (from 2.35)?

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**Answer:**

$$\frac{625 \text{ mg/L}}{31.25 \text{ mg/L}} = 20 \text{ decaf drinks} = 1 \text{ caf latte}$$

**2-38.** The average concentration of dissolved oxygen (DO) in the Shenandoah River was reported as 9.7 ppm<sub>m</sub> in 2006. What is the concentration in mg/L in the river water?

**Answer:**

$$9.7 \text{ ppm}_m \times \frac{1 \text{ mg/L}}{1 \text{ ppm}_m} = 9.7 \frac{\text{mg DO}}{\text{L}}$$

**2-39.** Table 2.18 includes typical constituents in water in mg/L. Complete the table by converting the concentrations to units given in the table, and find the mass in 1000 liters of water – the amount of water you would typically ingest over the course of a year.

Table 2.18: Typical constituents in water. Source: Tchobanoglous, G., Asano, T., Burton, F., Leverenz, H., Tsuchihashi, R. 2007. Water Reuse: Issues, Technologies, and Applications. McGraw-Hill. 1570 p. ISBN-13:978-0071459273.

**Answer:**

Constituent	mg/L	ppm	Molecular weight	mmol/L	Kg/year
Bicarbonate (HCO <sub>3</sub> )	75	75	61	1.23	0.075
Carbonate (CO <sub>3</sub> )	5	5	60	0.08	0.005
Chloride (Cl)	35	35	35.45	0.99	0.035
Sulfate (SO <sub>3</sub> )	27	27	80.06	0.34	0.027
Calcium (Ca)	11	11	40.08	0.27	0.011
Magnesium (Mg)	7	7	24.305	0.29	0.007
Potassium (K)	11	11	39.0983	0.28	0.011
Sodium (Na)	55	55	22.9898	2.39	0.055
Aluminum (Al)	0.2	0.2	26.9815	0.007	0.0002
Fluoride (F)	0.3	0.3	18.9984	0.016	0.0003

**2-40.** The total volume of the oceans on Earth is 1.35 x 10<sup>18</sup> m<sup>3</sup>. What are the masses of the following elements in the Ocean in units of kg?

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**Answer:**

$$V_{\text{oceans}} = 1.35 \times 10^{18} \text{ m}^3 \times \frac{1000 \text{ L}}{\text{m}^3} = 1.35 \times 10^{21} \text{ L}$$

- a. Oxygen, O, for which the concentration in the seawater is 857,000 ppm

$$C_o = 857,000 \text{ ppm} = 857,000 \frac{\text{mg O}}{\text{L}}$$

$$\text{From oxygen } \frac{857,000 \text{ mg O}}{\text{L}} \times 1.35 \times 10^{21} \text{ L} \times \frac{\text{kg}}{10^6 \text{ mg}}$$

$$M_o = 1.16 \times 10^{21} \text{ kg of oxygen in oceans}$$

- b. Hydrogen, H, for which the concentration in the seawater is 108,000 ppm

$$C_o = 108,000 \text{ ppm} = 108,000 \frac{\text{mg H}}{\text{L}}$$

$$\text{From oxygen } \frac{108,000 \text{ mg H}}{\text{L}} \times 1.35 \times 10^{21} \text{ L} \times \frac{\text{kg}}{10^6 \text{ mg}}$$

$$M_H = 1.46 \times 10^{20} \text{ kg of hydrogen in oceans}$$

- c. Sodium, Na, for which the concentration in the seawater is 10,500 ppm

$$C_{Na} = 10,500 \text{ ppm} = 10,500 \frac{\text{mg Na}}{\text{L}}$$

$$\text{From oxygen } \frac{10,500 \text{ mg Na}}{\text{L}} \times 1.35 \times 10^{21} \text{ L} \times \frac{\text{kg}}{10^6 \text{ mg}}$$

$$M_{Na} = 1.42 \times 10^{19} \text{ kg of sodium in oceans}$$

- 2-41.** What is the density of air in grams per cubic meter at 1 atm and 200°C?  
Assume the molecular weight of air is 28.967 grams/mole.

**Answer:**

$$n = m(\text{g})/MW(\text{g/mol})$$

let

$$m = 1 \text{ g}$$

$$V = 1 \text{ m}^3$$

$$P = 1 \text{ atm}$$

$$T = 200^\circ\text{C} = 273 + 200^\circ\text{C} = 473 \text{ K}$$

then

$$\frac{1m(\text{g})}{1V(\text{m}^3)} = \frac{P(MW)}{RT}$$

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$$\begin{aligned}
 R &= 8.205736 \times 10^{-5} \frac{\text{m}^3 \text{ atm}}{\text{K mol}} \\
 &= \frac{(1 \text{ atm}) \left( 28.967 \frac{\text{g}}{\text{mol}} \right)}{\left( 8.205736 \times 10^{-5} \frac{\text{m}^3 \text{ atm}}{\text{K mol}} \right) (473 \text{ K})} \\
 &= 746.32 \frac{\text{g}}{\text{m}^3} = 0.746 \frac{\text{kg}}{\text{m}^3}
 \end{aligned}$$

**2-42.** The reported value of carbon dioxide in the atmosphere in 2010 was approximately 385 ppm<sub>v</sub>. What is the concentration of carbon dioxide in the atmosphere in mg/m<sup>3</sup>?

**Answer:**

$$C_{\text{CO}_2} \left[ \frac{\text{mg}}{\text{m}^3} \right] = \frac{(385 \text{ ppm}_v) (44 \frac{\text{g}}{\text{mol}})}{24.5 \text{ ppm}_v - \text{g} - \text{m}^3 / \text{mol} - \text{mg}} = 691 \frac{\text{mg}}{\text{m}^3}$$

**2-43.** The mass of the oceans is  $1.4 \times 10^{21}$  kg. The concentration of potassium, K, in the oceans is 380 ppm<sub>m</sub>. What is the total mass of the potassium stored in the oceans in metric tonnes?

**Answer:**

$$\begin{aligned}
 380 \text{ ppm}_m &= 380 \frac{\text{mg}}{\text{kg}} \\
 \left( 380 \frac{\text{mg}}{\text{kg}} \right) (1.4 \times 10^{21} \text{ kg}) \\
 &= 5.32 \times 10^{23} \text{ mg} \\
 &= 5.32 \times 10^{17} \text{ kg} \\
 &= 5.32 \times 10^{14} \text{ metric tonnes}
 \end{aligned}$$

**2-44.** The mass of the Earth's troposphere, the lower part of the atmosphere, is approximately  $4.4 \times 10^{18}$  kg.

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- a. Use the ideal gas law to estimate volume of the troposphere in cubic meters at standard state ( $P = 1 \text{ atm}$ ,  $T = 298 \text{ K}$ ,  $R = 0.0821 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K}$ ). Note, the average molecular weight of air is 28.967 grams/mole.

**Answer:**

$$(P = 1 \text{ atm}, T = 298 \text{ K}, R = 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}})$$

$$PV = nRT$$

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{\left(\frac{m}{MW}\right)RT}{P} \\ &= \left(\frac{(4.4 \times 10^{18} \text{ kg}) \left(1000 \frac{\text{g}}{\text{kg}}\right) \left(0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}\right) \left(\frac{\text{m}^3}{1000 \text{ L}}\right)}{\left(28.96 \frac{\text{g}}{\text{mol}}\right) (1 \text{ atm})}\right) (298 \text{ K}) \\ &= 3.72 \times 10^{15} \text{ m}^3 \end{aligned}$$

- b. The average mass of water in the troposphere is  $1.3 \times 10^{13} \text{ kg}$ . Using your answer from above, calculate the concentration of water vapor in the troposphere in  $\text{mg}/\text{m}^3$ ?

**Answer:**

$$\begin{aligned} &\frac{(1.3 \times 10^{13} \text{ kg}) \left(10^6 \frac{\text{mg}}{\text{kg}}\right)}{3.72 \times 10^{15} \text{ m}^3} \\ &= 3500 \frac{\text{mg}}{\text{m}^3} \end{aligned}$$

- c. Using your answer from part b, what would be the concentration of water vapor in the troposphere in  $\text{ppm}_v$ ?

**Answer:**

$$\begin{aligned} C\left(\frac{\text{mg}}{\text{m}^3}\right) &= \frac{C(\text{ppm}_v)MW}{24.5} \\ C(\text{ppm}_v) &= \frac{C(\text{ppm}_v)24.5}{MW} \\ &= \frac{\left(3500 \frac{\text{mg}}{\text{m}^3}\right) (24.5)}{\left(28.96 \frac{\text{g}}{\text{mol}}\right)} \\ &= 2960 \text{ ppm}_v \end{aligned}$$

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2-45. Table 2.19 represents the National Ambient Air Quality Standards (NAAQS) air quality standard.

Table 2.19: National Ambient Air Quality Standards (Source: USEPA)

Pollutant	Averaging time	Level	Standard conditions ( $\mu\text{g}/\text{m}^3$ )	Denver in winter ( $\mu\text{g}/\text{m}^3$ )
Carbon Monoxide (CO)	8 - hour	9 ppm	10,286	9,060
	1 - hour	35 ppm	40,000	35,230
Nitrogen Dioxide (NO <sub>2</sub> )	1 - hour	100 ppb	188,000	166,000
	Annual	53 ppb	99,500	87,644
Ozone (O <sub>3</sub> )	8 - hour	0.075 ppm	147	129
Sulfur Dioxide (SO <sub>2</sub> )	1 - hour	75 ppb	196,000	172,556
	3 - hour	0.5 ppm	1,306	1,150

a. Express the standards in  $\mu\text{g}/\text{m}^3$  at 1 atm of pressure and 25°C

**Answer:**

From equation 2.20

$$C \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = \text{ppm}_v \times MW_i \times \frac{1,000 P}{RT}$$

- Carbon monoxide, CO with  $MW_{\text{CO}} = 28 \text{ g/mol}$

$$C_{\text{CO}} \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = (9 \text{ ppm}_v) (28 \text{ g/mol}) \left( \frac{1,000 (1 \text{ atm})}{(8.21 \times 10^{-5} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (298\text{K})} \right)$$

$$C_{\text{CO}} \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = 10,286 \mu\text{g}/\text{m}^3$$

- Nitrogen Dioxide, NO<sub>2</sub> with  $MW_{\text{NO}_2} = 46 \text{ g/mol}$

$$C_{\text{NO}_2} \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = \left( 100 \text{ ppb}_v \frac{1 \text{ ppm}_v}{1000 \text{ ppb}_v} \right) (46 \text{ g/mol}) \left( \frac{1,000 (1 \text{ atm})}{(8.21 \times 10^{-5} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (298\text{K})} \right)$$

$$C_{\text{NO}_2} \left[ \frac{\mu\text{g}}{\text{m}^3} \right] = 188,000 \mu\text{g}/\text{m}^3$$

- Ozone, O<sub>3</sub> with  $MW_{\text{O}_3} = 48 \text{ g/mol}$

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$$C_{O_3} \left[ \frac{ug}{m^3} \right] = (0.075 \text{ ppm}_v) (48 \text{ g/mol}) \left( \frac{1,000 (1 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (298K)} \right)$$

$$C_{O_3} \left[ \frac{ug}{m^3} \right] = 147 \text{ ug/m}^3$$

- Sulfur Dioxide, SO<sub>2</sub> with  $MW_{SO_2} = 64 \text{ g/mol}$

$$C_{SO_2} \left[ \frac{ug}{m^3} \right] = \left( 75 \text{ ppb}_v \frac{1 \text{ ppm}_v}{1000 \text{ ppb}_v} \right) (64 \text{ g/mol}) \left( \frac{1,000 (1 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (298K)} \right)$$

$$C_{SO_2} \left[ \frac{ug}{m^3} \right] = 196,000 \text{ ug/m}^3$$

- b. At the elevation of Denver, the pressure is about 0.82 atm. Express the standards in  $\mu\text{g}/\text{m}^3$  at that pressure and temperature of 5°C.

**Answer:**

- Carbon monoxide, CO with  $MW_{CO} = 28 \text{ g/mol}$

$$C_{CO_{Denver}} \left[ \frac{ug}{m^3} \right] = (9 \text{ ppm}_v) (28 \text{ g/mol}) \left( \frac{1,000 (0.82 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (278K)} \right)$$

$$C_{CO_{Denver}} \left[ \frac{ug}{m^3} \right] = 9,060 \text{ ug/m}^3$$

- Nitrogen Dioxide, NO<sub>2</sub> with  $MW_{NO_2} = 46 \text{ g/mol}$

$$C_{NO_2_{Denver}} \left[ \frac{ug}{m^3} \right] = \left( 100 \text{ ppb}_v \frac{1 \text{ ppm}_v}{1000 \text{ ppb}_v} \right) (46 \text{ g/mol}) \left( \frac{1,000 (0.82 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (278K)} \right)$$

$$C_{NO_2_{Denver}} \left[ \frac{ug}{m^3} \right] = 166,000 \text{ ug/m}^3$$

- Ozone, O<sub>3</sub> with  $MW_{O_3} = 48 \text{ g/mol}$

$$C_{O_3_{Denver}} \left[ \frac{ug}{m^3} \right] = (0.075 \text{ ppm}_v) (48 \text{ g/mol}) \left( \frac{1,000 (0.82 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (278K)} \right)$$

$$C_{O_3_{Denver}} \left[ \frac{ug}{m^3} \right] = 129 \text{ ug/m}^3$$

- Sulfur Dioxide, SO<sub>2</sub> with  $MW_{SO_2} = 64 \text{ g/mol}$

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$$C_{SO_2_{DENVER}} \left[ \frac{ug}{m^3} \right] = \left( 75 \text{ ppb}_v \frac{1 \text{ ppm}_v}{1000 \text{ ppb}_v} \right) (64 \text{ g/mol}) \left( \frac{1,000 (0.82 \text{ atm})}{\left( 8.21 \times 10^{-5} \frac{m^3 \cdot atm}{mol \cdot K} \right) (278 K)} \right)$$
$$C_{SO_2_{DENVER}} \left[ \frac{ug}{m^3} \right] = 172,556 \text{ ug/m}^3$$

**2-46.** Use Henry's law to calculate the concentration of dissolved carbon dioxide (or inorganic carbonates) in a raindrop during the Ordovician Epoch. The atmospheric concentration of carbon dioxide were 2240 ppm<sub>v</sub> CO<sub>2</sub>. Assuming pressure at sea level was 1 atm and the water temperature was 20°C.

**Answer:**

The partial pressure of CO<sub>2</sub>

$$= \frac{2240}{10^6} (1 \text{ atm})$$
$$= 0.00224 \text{ atm}$$

Assume  $T = 25^\circ\text{C}$

$$K_H = 0.033363$$

$$C \left( \frac{\text{mol}}{\text{L}} \right) = \left( 0.033363 \frac{\text{mol}}{\text{L-atm}} \right) (0.00224 \text{ atm})$$
$$= 8.77 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$
$$= \left( 8.77 \times 10^{-5} \frac{\text{mol}}{\text{L}} \right) \left( \frac{44 \text{ g}}{\text{mol}} \right) \left( \frac{1000 \text{ mg}}{\text{g}} \right)$$
$$= 3.86 \frac{\text{mg}}{\text{L}}$$



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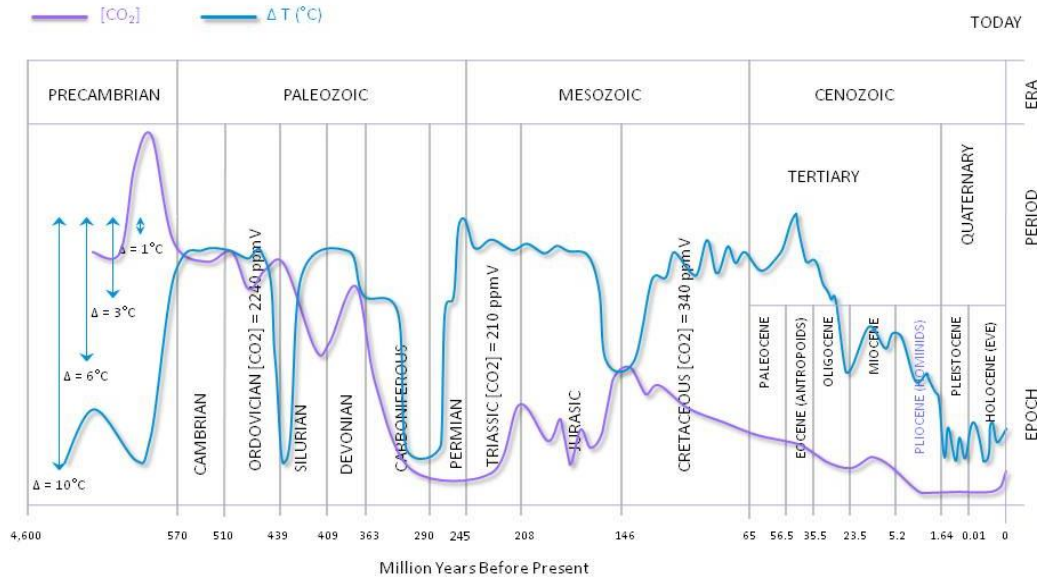


Figure 2.26: Fluctuation of carbon dioxide and temperature over geological timescales

Source: Nasif Nahle. 2007. Cycles of Global Climate Change. Biology Cabinet Journal Online. Article no 295.

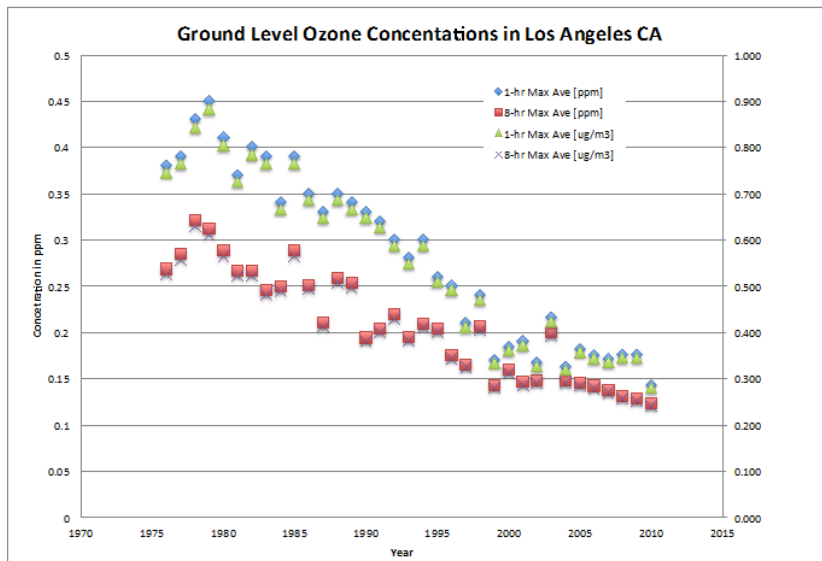
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**2-47.** The data shown in Table 2.20 were collected for ozone levels in the Los Angeles, CA air basin. Plot the data recorder below in Excel in ppm and  $\mu\text{g}/\text{m}^3$ . Identify the years LA was not in compliance with the NAAQS standards.

Table 2.20: Ozone concentrations reported in Los Angeles, CA (Historic Ozone Air Quality Trends, South Coast Air Quality Management District, <http://www.aqmd.gov/smog/o3trend.html>)

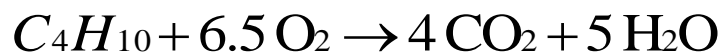
Year	Basin Maximum 1-hour average (ppm)	Basin Maximum 8-hour Average (ppm)	Year	Basin Maximum 1-hour average(ppm)	Basin Maximum 8-hour Average(ppm)
1976	0.38	0.268	1994	0.30	0.209
1977	0.39	0.284	1995	0.26	0.204
1978	0.43	0.321	1996	0.25	0.175
1979	0.45	0.312	1997	0.21	0.165
1980	0.41	0.288	1998	0.24	0.206
1981	0.37	0.266	1999	0.17	0.143
1982	0.40	0.266	2000	0.184	0.159
1983	0.39	0.245	2001	0.190	0.146
1984	0.34	0.249	2002	0.167	0.148
1985	0.39	0.288	2003	0.216	0.200
1986	0.35	0.251	2004	0.163	0.148
1987	0.33	0.210	2005	0.182	0.145
1988	0.35	0.258	2006	0.175	0.142
1989	0.34	0.253	2007	0.171	0.137
1990	0.33	0.194	2008	0.176	0.131
1991	0.32	0.204	2009	0.176	0.128
1992	0.30	0.219	2010	0.143	0.123
1993	0.28	0.195			

**Answer:**



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**2-48.** Balance the equation the following reaction representing the combustion of butane:



a. How many moles of oxygen are required to burn 1 mol of butane?

**Answer:**

6.5 moles of  $O_2$

b. How many grams of oxygen are required to burn 1 kg of butane?

$$1 \text{ kg } C_4H_{10} \times \frac{\text{mol } C_4H_{10}}{0.058 \text{ kg}} \times \frac{6.5 \text{ mol } O_2}{1 \text{ mol } C_4H_{10}} \times \frac{32 \text{ g } O_2}{\text{mol } O_2} = 3586 \text{ g } O_2$$

**Answer:**

c. At standard temperature and pressure, what volume of oxygen would be required to burn 100 g of butane?

**Answer:**

$$100 \text{ g butane} \times \frac{1 \text{ mol } C_4H_{10}}{58 \text{ g } C_4H_{10}} \times \frac{6.5 \text{ mol } O_2}{1 \text{ mol } C_4H_{10}} = 11.2 \text{ mol } O_2$$

d. What volume of air at STP is required to burn 100 g of butane?

**Answer:**

$$V_{O_2} = \frac{nRT}{P} = \frac{(11.2 \text{ mol})(298 \text{ K})}{(1 \text{ atm})} \times (8.205 \times 10^{-5} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}) = 0.274 \text{ m}^3$$

$$\frac{V_{O_2}}{V_{air}} = \frac{P_{O_2}}{P_{air}}$$

$$V_{air} = \frac{(0.274 \text{ m}^3)(1 \text{ atm})}{(0.21 \text{ atm } O_2)} = 1.31 \text{ m}^3 \text{ air}$$

**2-49.** What is the molarity of 25 g of glucose ( $C_6H_{12}O_6$ ) dissolved in 1 liter of water?

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Answer:

	<u>#</u>		<u>MW</u>		
C	6	x	12	=	72
H	12	x	1	=	12
O	6	x	6	=	<u>36</u>
	180		$\frac{\text{g}}{\text{mol}}$		

$$c \left( \frac{\text{mol}}{\text{L}} \right) = \frac{25 \text{ grams}}{\left( 180 \frac{\text{g}}{\text{mol}} \right) (1 \text{ Liter})} = 0.14 \text{ M}$$

**2-50.** Wine contains about 15% ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , by volume. If the density of ethyl alcohol is 0.79 kg/L, what is its molarity in wine? (Wine is an aqueous solution – that is to say most of the rest of the volume of wine consists of water.)

Answer:

$$0.15\% \text{ of } 1.0 \text{ ethyl alcohol} = 0.15 \text{ L} \times 0.79 \frac{\text{kg}}{\text{L}}$$

$$1 \text{ liter of wine} \times \frac{0.15 \text{ ethanol}}{\text{L wine}} \times \frac{0.79 \text{ kg ethanol}}{\text{L ethanol}} \times \frac{1000 \text{ g}}{\text{L}} = 118.5 \text{ g of ethanol}$$

$$118.5 \text{ g} \times \frac{\text{mol ethanol}}{46 \text{ g}} = 2.58 \text{ mol per liter} = 2.58 \text{ M}$$

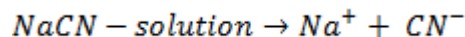
**2-51.** A waste stream of 20,000 gal/min contains 270 mg/L of cyanide as NaCN.

a. What is the ionic strength of the solution in (mmol/l)

Answer:

$$MW_{\text{NaCN}} = (23 + 12 + 14) = 49 \frac{\text{g}}{\text{mol}} = 49 \frac{\text{mg}}{\text{mmol}}$$

$$270 \frac{\text{mg}}{\text{L}} \times \frac{\text{mmol}}{49 \text{ mg}} = 5.51 \frac{\text{mmol}}{\text{L}}$$



-there is 1 positive and 1 negative ion associated with each mole of NaCN

$$I = \frac{1}{2} \sum c_i z_i^2$$

$$I = \frac{1}{2} \left( 5.51 \frac{\text{mmol}}{\text{L}} (+1)^2 + 5.51 \frac{\text{mmol}}{\text{L}} (-1)^2 \right)$$

$$I = 5.51 \frac{\text{mmol}}{\text{L}} = 5.51 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

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- b. What is the appropriate activity coefficient for dissolved cyanide, CN<sup>-</sup> in this solution if the sodium cyanide is the only dissolved species? (Use the Güntelberg approximation.)

**Answer:**

$$\begin{aligned} \log(\gamma) &= -\frac{(0.51z_i^2I^{0.5})}{(1+I^{0.5})} \\ &= -\frac{(0.51(1)^2(5.51 \times 10^{-3} \frac{\text{mol}}{\text{L}})^{0.5})}{(1+(5.51 \times 10^{-3} \frac{\text{mol}}{\text{L}})^{0.5})} \\ &= 0.92 \end{aligned}$$

- 2-52.** Table 2.21 represents a “total analysis” of wastewater has been reported. Note that the pH is not given.

Table 2.21: Data for analysis of wastewater in Problem 2.52.

Cation	Concentration [mg/L]	Molar Mass	Anion	Concentration [mg/L]	Molar Mass
NH <sub>3</sub>	0.08	as N	F <sup>-</sup>	21.2	as F
Na <sup>+</sup>	18.3	as Na	Cl <sup>-</sup>	24.1	as Cl
K <sup>+</sup>	18.3	as K	HCO <sub>3</sub> <sup>-</sup>	15	as C
Ca <sup>2+</sup>	1.7	as CaCO <sub>3</sub>	SO <sub>4</sub> <sup>-2</sup>	20	as SO <sub>4</sub>
			NO <sub>3</sub> <sup>-</sup>	2.0	as N
			NO <sub>2</sub> <sup>-</sup>	0.008	as N

- a. Do a charge balance analysis on the data to see if such a solution would be electrically neutral

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**Answer:**

### Wastewater Composition

Cations	Concentration of molar mass (mg/L)	Molar Weight (mg/mmol)	Concentration charge (mmol/L)	$z_i$	meq/L
NH <sub>3</sub>	0.08 as N	14	0.00571429	0	0
Na <sup>+</sup>	18.3 as Na	23	0.79565217	1	0.79565217
K <sup>+</sup>	18.3 as K	38	0.48157895	1	0.48157895
Ca <sup>2+</sup>	1.7 as CaCO <sub>3</sub>	100	0.017	2	0.034
<b>Sum Cations</b>					1.31123112
<b>Anions</b>					
F <sup>-</sup>	21.2 as F	19	1.11578947	-1	-1.1157895
Cl <sup>-</sup>	24.1 as Cl	35.4	0.68079096	-1	-0.680791
HCO <sub>3</sub> <sup>3-</sup>	15 as C	12	1.25	-1	-1.25
SO <sub>4</sub> <sup>2-</sup>	20 as SO <sub>4</sub>	96	0.20833333	-2	-0.4166667
NO <sub>3</sub> <sup>-</sup>	2 as N	14	0.14285714	-1	-0.1428571
NO <sub>2</sub> <sup>-</sup>	0.008 as N	14	0.00057143	-1	-0.0005714
<b>Sum Anions</b>					-3.6066757
<b>Difference between anions and cations</b>					2.29544458 meq/L

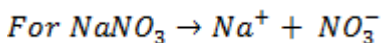
- b. If H<sup>+</sup> and OH<sup>-</sup> are the only ions missing from the analysis, what must their concentration be? i.e. what is the pH and pOH?

**Answer:**

$$\begin{aligned}
 [H^+] &= 2.295 \frac{\text{meq}}{\text{L}} \times \frac{1 \text{ mmol}}{1 \text{ meq}} \times \frac{\text{mol}}{1000 \text{ mmol}} \\
 &= 0.002295 \frac{\text{mol}}{\text{L}} \\
 \text{pH} &= -\log[H^+] = -\log[0.002295] = 2.64
 \end{aligned}$$

**2-53.** Calculate the activity coefficient and activity of each ion in a solution containing 300mg/l NaNO<sub>3</sub> and 150 mg/L CaSO<sub>4</sub>.

**Answer:**



-1 mole of ions forms with each mole of the salt

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$$300 \frac{\text{mg}}{\text{L}} \text{NaNO}_3 \times \frac{\text{g}}{1000 \text{mg}} \times \frac{\text{mol}}{(85 \text{g})} = 0.00353 \frac{\text{mol}}{\text{L}}$$

$$0.00353 \frac{\text{mol}}{\text{L}} \text{NaNO}_3 = 0.00353 \frac{\text{mol}}{\text{L}} \text{Na}^+ = 0.00353 \frac{\text{mol}}{\text{L}} \text{NO}_3^-$$

-for  $\text{Na}^+$  &  $\text{NO}_3^-$  there is 1 charge per mole

$$1 \text{ eq. Na}^+ = 1 \text{ mol Na}^+$$

For  $\text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$

$$150 \frac{\text{mg}}{\text{L}} \text{CaSO}_4 \times \frac{\text{g}}{1000 \text{ mg}} \times \frac{\text{mol}}{136 \text{ g}} = 0.0011 \frac{\text{mol}}{\text{L}} \text{CaSO}_4 = 0.0011 \frac{\text{mol}}{\text{L}} \text{Ca}^{2+} = 0.0011 \frac{\text{mol}}{\text{L}} \text{SO}_4^{2-}$$

For  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  there are 2 eq/mol

$$\text{Ca}^{2+} = 0.0011 \frac{\text{mol}}{\text{L}} \times \frac{2 \text{ eq}}{\text{mol}} = 0.0022 \frac{\text{eq}}{\text{L}}$$

$$\text{SO}_4^{2-} = 0.0011 \frac{\text{mol}}{\text{L}} \times 2 \frac{\text{eq}}{\text{mol}} = 0.0022 \frac{\text{eq}}{\text{L}}$$

$$I = \frac{1}{2} \left( [\text{Ca}^{2+}][Z_{\text{Ca}^{2+}}]^2 + [\text{Na}^{2+}][Z_{\text{Na}^+}]^2 + [\text{SO}_4^{2-}][Z_{\text{SO}_4^{2-}}]^2 + [\text{NO}_3^-][Z_{\text{NO}_3^-}]^2 \right)$$

$$= \frac{1}{2} \left( (0.0011)(2)^2 + (0.00353)(1)^2 + (0.0011)(-2)^2 + (0.00853)(-1)^2 \right)$$

$$= 0.0079 \frac{\text{mol}}{\text{L}}$$

$$\log(\gamma) = \frac{-(0.51 z_i^2 I^{0.5})}{(1 + I^{0.5})}$$

$$\log(\gamma_1) = \frac{-(0.51(1)^2(0.0079)^{0.5})}{1 + (0.0079)^{0.5}}$$

$$\log(\gamma_1) = \gamma_{\text{Na}^+} = \gamma_{\text{NO}_3^-} = 0.91$$

$$\log(\gamma_2) = \frac{-(0.51(2)^2(0.0079)^{0.5})}{1 + (0.0079)^{0.5}}$$

$$\gamma_2 = \gamma_{\text{CO}^{2+}} = \gamma_{\text{SO}_4^{2-}} = 0.68$$

**2-54.** The major dissolved species in the Colorado River near Phoenix are given in mg/l in the table below.

Table 2.22: Dissolved ions in the Colorado River. Source: US Department of Interior, 2001.

Cation	Concentration [mg/L]	Molar Mass	Anion	Concentration [mg/L]	Molar Mass
$\text{Ca}^{2+}$	83	as Ca	$\text{SO}_4^{2-}$	250	as $\text{SO}_4$
$\text{K}^+$	5.1	as K	$\text{Cl}^-$	88	as Cl
$\text{H}^+$	0.000065	as H	$\text{HCO}_3^-$	135	as $\text{CaCO}_3$

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- a. Express the concentration of  $\text{Ca}^{2+}$  in the Colorado River in moles of  $\text{Ca}^{2+}$  per liter and in milligrams per liter as  $\text{CaCO}_3$ .

**Answer:**

$$77 \frac{\text{mg Ca}^{2+}}{\text{L}} \times \frac{\text{mol Ca}^{2+}}{40,000 \text{mg}} = 0.0019 \text{ mol/L}$$

$$0.0019 \frac{\text{mol Ca}^{2+}}{\text{L}} \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol Ca}^{2+}} \times \frac{100 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \times \frac{1000 \text{ mg}}{\text{g}} = 192 \frac{\text{mg CaCO}_3}{\text{L}}$$

- b. The concentration of  $\text{Na}^+$  is not given in the table. Assuming that  $\text{Na}^+$  is the only significant species missing from the analysis, compute its value based on the electroneutrality requirement. Note: the  $\text{HCO}_3^-$  concentration is expressed in terms of  $\text{CaCO}_3$  hardness.

**Answer:**

- c. Calculate the total hardness, carbonate hardness and non-carbonate hardness for the Colorado River using the data in the table above.

**Answer:**

*The dipotic ions from table 2.22 consist only of  $\text{Ca}^{2+}$*

$$\frac{83 \text{ mg Ca}^{2+}}{\text{L}} \times \frac{100 \text{ mg CaCO}_3}{40 \text{ mg Ca}^{2+}} = 207.5 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\therefore \text{total hardness} = 207.5 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Carbonate Hardness is due to the  $\text{HCO}_3^-$  ions*

$$\frac{135 \text{ mg as C}}{\text{L}} \times \frac{100 \text{ mg CaCO}_3}{12 \text{ mg C}} = 1125 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*since carbonate concentration > total hardness,  
carbonate hardness = total hardness =  $207.5 \frac{\text{mg}}{\text{L}}$*

*and non-carbonate hardness =  $\emptyset$*



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2-55. For the water date shown in Table 4.20. Find the following information

Table 2.23: Concentration of major dissolved ions in various water bodies

Ion	Snake River	Mississippi River	Lower Congo, Kinshasa	Ganges River	Dead Sea
<b>Cation</b>	<b>Concentration [mg/L]</b>				
Ca <sup>2+</sup>	16.1	162	10.8	88	63,000
Mg <sup>2+</sup>	2.91	45	3.9	19	168,000
K <sup>+</sup>	4.14	3		2.3	7527
Na <sup>+</sup>	28.4	21	14.2	6.4	35,000
Fe <sup>2+</sup>	12				
<b>Anions</b>					
Cl <sup>-</sup>	15.4	54	6.1	5.7	207,000
F <sup>-</sup>	2.1				
HCO <sub>3</sub> <sup>-</sup>	73	124		104	244
SO <sub>4</sub> <sup>2-</sup>	25.2	100	7.8	371	2110
<b>Reference:</b>	Clark et. al., 2004	Maybeck et. al., 1989	Visser, S. A. and Villeneuve, J.P. (1975)	Maybeck et. al., 1989	Maybeck et. al., 1989

a. For Snake River

i) Calculate the ionic strength

**Answer:**

Ion	$C_{mL}(mg/L)$	$MW(g/mol)$	$z_i$	$C_i(mmol/L)$	$C_i z_i^2$
Ca <sup>2+</sup>	16.1	40.08	2	0.402	1.607
Mg <sup>2+</sup>	2.91	24.305	2	0.120	0.479
K <sup>+</sup>	4.14	39.10	1	0.106	0.106
Na <sup>+</sup>	28.4	22.99	1	1.235	1.235
Fe <sup>2+</sup>	12	55.85	2	0.215	0.859
Cl <sup>-</sup>	15.4	35.45	1	0.434	0.434
F <sup>-</sup>	2.1	19.00	1	0.111	0.111
HCO <sub>3</sub> <sup>-</sup>	73	61.02	1	1.196	1.196
SO <sub>4</sub> <sup>2-</sup>	25.2	96.02	2	0.262	1.049

$$\Sigma = 7.077$$

$$I = 3.54 \frac{Meq}{L}$$

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ii) Calculate the activity coefficient

**Answer:**

$$\gamma_i = 10^{-0.51z_i^2 I^{0.5}} = 10^{-0.51(1)^2(0.00354)^{0.5}}$$

$$\gamma_1 = 0.93$$

$$\gamma_2 = 0.76$$

b. For the Mississippi River

i) Calculate the ionic strength

**Answer:**

Ion	$C_{mL}(mg/L)$	MW(g/mol)	$z_i$	$C_i(mmol/L)$	$C_i z_i^2$
Ca <sup>2+</sup>	162	40.08	2	3.97	15.88
Mg <sup>2+</sup>	45	24.305	2	1.85	7.4
K <sup>+</sup>	3	39.10	1	0.077	0.077
Na <sup>+</sup>	21	22.99	1	0.913	0.913
Cl <sup>-</sup>	54	35.45	1	1.52	1.52
HCO <sub>3</sub> <sup>-</sup>	124	61.02	1	2.03	2.03
SO <sub>4</sub> <sup>2-</sup>	100	96.02	2	1.04	4.16

$$\Sigma = 31.98$$

$$I = 15.99 \frac{M_{eq}}{L}$$

ii) Calculate the activity coefficient

**Answer:**

$$\gamma_i = 10^{-0.51z_i^2 I^{0.5}} = 10^{-0.51(1)^2(0.01599)^{0.5}}$$

$$\gamma_1 = 0.86$$

$$\gamma_2 = 0.55$$

c. For the Lower Congo River

i) Calculate the ionic strength

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**Answer:**

Ion	$C_{mL}(\text{mg/L})$	MW(g/mol)	$z_i$	$C_i(\text{mmol/L})$	$C_i z_i^2$
$\text{Ca}^{2+}$	10.8	40.08	2	0.270	1.077
$\text{Mg}^{2+}$	3.9	24.305	2	0.161	0.322
$\text{Na}^+$	14.2	22.99	1	0.618	0.618
$\text{Cl}^-$	6.1	35.45	1	0.172	0.172
$\text{SO}_4^{2-}$	7.8	96.02	2	0.081	0.324
$\Sigma = 2.513$					

$$I = 1.257 \frac{\text{Meq}}{\text{L}}$$

ii) Calculate the activity coefficient

**Answer:**

$$\gamma_i = 10^{-0.51 z_i^2 I^{0.5}} = 10^{-0.51(1)^2(0.001257)^{0.5}}$$

$$\gamma_1 = 0.96$$

$$\gamma_2 = 0.85$$

d. For the Dead Sea

i) Calculate the ionic strength

**Answer:**

Ion	$C_{mL}(\text{mg/L})$	MW(g/mol)	$z_i$	$C_i(\text{mmol/L})$	$C_i z_i^2$
$\text{Ca}^{2+}$	63,000	40.08	2	1,571.86	6,287.44
$\text{Mg}^{2+}$	168,000	24.305	2	6,912.16	27,648.64
$\text{K}^+$	7,527	39.10	1	192.5	192.5
$\text{Na}^+$	35,000	22.99	1	1,522.4	1,522.4
$\text{Cl}^-$	207,000	35.45	1	5,839.21	5,839.21
$\text{HCO}_3^-$	244	61.02	1	4.00	4.00
$\text{SO}_4^{2-}$	2,110	96.02	2	21.97	87.88
$\Sigma = 41,582.07$					

$$I = 20,791.035 \frac{\text{Meq}}{\text{L}}$$

ii) Calculate the activity coefficient

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**Answer:**

$$\gamma_i = 10^{-0.51z_i^2 t^{0.5}} = 10^{-0.51(1)^2(20.791035)^{0.5}}$$

$$\gamma_1 = 0.01$$

$$\gamma_2 = 5.0 \times 10^{-10}$$

**2-56.** Calculate the total hardness, carbonate hardness and non-carbonate hardness for the Ganges River using the data in Table 2.23.

**Answer:**

*Dipotic ions are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$*

$$88 \frac{\text{mg Ca}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{40 \text{mg as Ca}^{2+}} = 219.6 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$19 \frac{\text{mg Mg}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{24.3 \text{mg as Mg}^{2+}} = 170.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{total hardness} = 298 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Carbonate contribution to hardness is due to  $\text{HCO}_3^-$*

$$104 \frac{\text{mg HCO}_3^-}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{61 \text{mg as HCO}_3^-} = 170.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Since carbonate comes as  $\text{CaCO}_3 < \text{total hardness}$*

$$\text{carbonate hardness} = 170 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{Non carbonate hardness} = 298 \frac{\text{mg}}{\text{L}} - 170 \frac{\text{mg}}{\text{L}} = 127.3 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

**2-57.** Calculate the total hardness, carbonate hardness and non-carbonate hardness for the Mississippi River using the data in Table 2.23.

**Answer:**

*Dipotic ions are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$*

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$$162 \frac{\text{mg Ca}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{40 \text{mg as Ca}^{2+}} = 404 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$45 \frac{\text{mg Mg}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{24.3 \text{mg as Mg}^{2+}} = 185.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{total hardness} = 589 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

Carbonate contribution to hardness is due to  $\text{HCO}_3^-$

$$124 \frac{\text{mg HCO}_3^-}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{61 \text{mg as HCO}_3^-} = 203.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

Since carbonate comes as  $\text{CaCO}_3 < \text{total hardness}$

$$\text{carbonate hardness} = 203.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{Non carbonate hardness} = 298 \frac{\text{mg}}{\text{L}} - 170 \frac{\text{mg}}{\text{L}} = 386 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

**2-58.** Calculate the total hardness, carbonate hardness and non-carbonate hardness for the Dead Sea using the data in Table 2.23.

**Answer:**

Dipotic ions are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$

$$63,000 \frac{\text{mg Ca}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{40 \text{mg as Ca}^{2+}} = 157,000 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$168,080 \frac{\text{mg Mg}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{24.3 \text{mg as Mg}^{2+}} = 691,000 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{total hardness} = 848,000 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

Carbonate contribution to hardness is due to  $\text{HCO}_3^-$

$$244 \frac{\text{mg HCO}_3^-}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{61 \text{mg as HCO}_3^-} = 400 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

Since carbonate comes as  $\text{CaCO}_3 < \text{total hardness}$

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$$\text{carbonate hardness} = 400 \frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3$$

$$\text{Non carbonate hardness} = 848,000 \frac{\text{mg}}{\text{L}} - 400 \frac{\text{mg}}{\text{L}} = 848,000 \frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3$$

**2-59.** The following laboratory data has been recorded for a one hundred milliliter sample of water. Calculate the concentration of total solids, total dissolved solids, and total volatile solids in mg/L.

Description	Unit	Recorded Value
Sample size	ml	100
Mass of evaporating dish	g	34.9364
Mass of evaporating dish plus residue after evaporating at 105 °C	g	34.9634
Mass of evaporating dish plus residue after evaporating at 550 °C	g	34.9606
Mass of Whatman paper filter	g	1.6722
Mass of Whatman paper filter after evaporating at 105 °C	g	1.6834
Mass of Whatman paper filter after evaporating at 550 °C	g	1.6773

**Answer:**

$$\text{Total Dissolved Solids} = \frac{(34.9634 - 34.9364) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 270 \text{ mg/L}$$

$$\text{Fixed Dissolved Solids} = \frac{(34.9606 - 34.9364) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 242 \text{ mg/L}$$

$$\text{Volatile Dissolved Solids} = 270 \text{ mg/L} - 242 \text{ mg/L} = 28 \text{ mg/L}$$

$$\text{Suspended Solids} = \frac{(1.6834 - 1.6722) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 112 \text{ mg/L}$$

$$\text{Fixed Suspended Solids} = \frac{(1.6773 - 1.6722) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 51 \text{ mg/L}$$

$$\text{Volatile Suspended Solids} = 112 \text{ mg/L} - 51 \text{ mg/L} = 61 \text{ mg/L}$$

$$\text{Total Solids} = 270 \text{ mg/L} + 112 \text{ mg/L} = 382 \text{ mg/L}$$

$$\text{Total Volatile Solids} = 28 \text{ mg/L} + 61 \text{ mg/L} = 89 \text{ mg/L}$$

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**2-60.** The following laboratory data has been recorded for a one liter sample of water. Calculate the concentration of total solids, total dissolved solids, and total volatile solids in mg/L.

Description	Unit	Recorded Value
Sample size	ml	1000
Mass of evaporating dish	g	62.1740
Mass of evaporating dish plus residue after evaporating at 105 °C	g	62.9712
Mass of evaporating dish plus residue after evaporating at 550 °C	g	62.8912
Mass of Whatman paper filter	g	1.4671
Mass of Whatman paper filter after evaporating at 105 °C	g	1.7935
Mass of Whatman paper filter after evaporating at 550 °C	g	1.6188

**Answer:**

$$\text{Total Dissolved Solids} = \frac{(62.9712 - 62.1740) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 7,972 \text{ mg/L}$$

$$\text{Fixed Dissolved Solids} = \frac{(62.8912 - 62.1740) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 7,172 \text{ mg/L}$$

$$\text{Volatile Dissolved Solids} = 7,972 \text{ mg/L} - 7,172 \text{ mg/L} = 800 \text{ mg/L}$$

$$\text{Suspended Solids} = \frac{(1.7935 - 1.4671) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 3,264 \text{ mg/L}$$

$$\text{Fixed Suspended Solids} = \frac{(1.6188 - 1.4671) \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1000 \text{ mg}}{\text{g}} = 1,517 \text{ mg/L}$$

$$\text{Volatile Suspended Solids} = 3,264 \text{ mg/L} - 1,517 \text{ mg/L} = 1,747 \text{ mg/L}$$

$$\text{Total Solids} = 7,972 \text{ mg/L} + 3,264 \text{ mg/L} = 11,236 \text{ mg/L}$$

$$\text{Total Volatile Solids} = 800 \text{ mg/L} + 1,747 \text{ mg/L} = 2,547 \text{ mg/L}$$

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**2-61.** Find the hardness of the following groundwater for the well water sample from a well in Pennsylvania.

Table 2.24: Ions in spring water in Pennsylvania wells. Source: Flippo, H. N. Jr. (1974) Springs of Pennsylvania. United States Department of the Interior, Geological Survey, Harrisburg, PA, USA.

Water Source	Concentration of ions [mg/L]						
	Cations			Anions			
	[Na <sup>+</sup> ]	[Ca <sup>2+</sup> ]	[Mg <sup>2+</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[Cl <sup>-</sup> ]	[HCO <sub>3</sub> <sup>-</sup> ]
A. Spring Mf 1	16	51	15	25	24	12	197
B. Spring Ln 12	4.7	48	7.3	25	26	9.2	114

**Answer:**

*Dipotic ions are Ca<sup>2+</sup> and Mg<sup>2+</sup>*

$$51 \frac{\text{mg Ca}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{40 \text{mg as Ca}^{2+}} = 127 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$15 \frac{\text{mg Mg}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{24.3 \text{mg as Mg}^{2+}} = 162.4 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{total hardness} = 189 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Carbonate contribution to hardness is due to HCO<sub>3</sub><sup>-</sup>*

$$197 \frac{\text{mg HCO}_3^-}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{61 \text{mg as HCO}_3^-} = 323 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Since carbonate comes as CaCO<sub>3</sub> > total hardness*

$$\text{carbonate hardness} = 323 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Non carbonate hardness = ∅*



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**2-62.** Find the hardness of the following groundwater for the well water sample from a well in Pennsylvania, as assigned by your instructor.

Table 2.24: Ions in spring water in Pennsylvania wells. Source: Flippo, H. N. Jr. (1974) Springs of Pennsylvania. United States Department of the Interior, Geological Survey, Harrisburg, PA, USA.

Water Source	Concentration of ions [mg/L]						
	Cations			Anions			
	[Na <sup>+</sup> ]	[Ca <sup>2+</sup> ]	[Mg <sup>2+</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[Cl <sup>-</sup> ]	[HCO <sub>3</sub> <sup>-</sup> ]
Spring Ln 12	4.7	48	7.3	25	26	9.2	114

*Diprotic ions are Ca<sup>2+</sup> and Mg<sup>2+</sup>*

$$48 \frac{\text{mgCa}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{40 \text{mg as Ca}^{2+}} = 120 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$7.3 \frac{\text{mgMg}^{2+}}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{24.3 \text{mg as Mg}^{2+}} = 30 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

$$\text{Total Hardness} = 150 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Carbonate contribution to hardness is due to HCO<sub>3</sub><sup>-</sup>*

$$114 \frac{\text{mgHCO}_3^-}{\text{L}} \times \frac{100 \text{mg as CaCO}_3}{61 \text{mg as Ca}^{2+}} = 186 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Since carbonate comes as CaCO<sub>3</sub> > total hardness*

$$\text{Carbonate Hardness} = \text{Total Hardness} = 150 \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3$$

*Non carbonate hardness = ∅*

**2-63.** Find the hydrogen concentration and the hydroxide concentration in tomato juice having a pH of 5.

**Answer:**

$$\text{pH} = -\log[\text{H}^+] = 5$$

$$[\text{H}^+] = 10^{-5} \frac{\text{mol}}{\text{L}}$$

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$$pOH = 14 - pH = 14 - 5 = 9$$

$$pOH = -\log[OH^-] = 9$$

$$[OH^-] = 10^{-9} \frac{\text{mol}}{\text{L}}$$

2-64. What is  $-\log [H^+]$  of water in an estuary at pH 8.2 and  $I = 0.05$ ?

**Answer:**

$$\begin{aligned} pH &= -\log\{H^+\} \\ \{H^+\} &= 10^{-8.2} = [H^+]j_H^+ \\ \log(j_H^+) &= -0.5 z_i^2 I^{1/2} \\ j_H^+ &= 10^{-0.5(1)^2(0.05)^{1/2}} = 0.773 \\ [H^+] &= 10^{-8.2}/0.773 = 8.16 \times 10^{-9} \\ [H^+] &= 10^{-8.1} \\ \log[H^+] &= 8.1 \end{aligned}$$

2-65. Calculate the normality of the following solutions:

- a. 36.5 g/L hydrochloric acid [HCl]

**Answer:**

$$\frac{36.5 \text{ g HCl}}{\text{L}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \times \frac{1 \text{ eq}}{1 \text{ mol HCl}} = 1 \text{ N}$$

- b. 80 g/L sodium hydroxide [NaOH]

**Answer:**

$$\frac{80 \text{ g NaOH}}{\text{L}} \times \frac{1 \text{ mol NaOH}}{40 \text{ g NaOH}} \times \frac{1 \text{ eq}}{1 \text{ mol NaOH}} = 2 \text{ N}$$

- c. 9.8 g/L sulfuric acid [H<sub>2</sub>SO<sub>4</sub>]

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**Answer:**

$$\frac{9.8 \text{ g H}_2\text{SO}_4}{\text{L}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98 \text{ g H}_2\text{SO}_4} \times \frac{2 \text{ eq}}{1 \text{ mol H}_2\text{SO}_4} = 0.2 \text{ N}$$

d. 9.0 g/L acetic acid [CH<sub>3</sub>COOH]

**Answer:**

$$\frac{9.0 \text{ g HAc}}{\text{L}} \times \frac{1 \text{ mol HAc}}{60 \text{ g HAc}} \times \frac{1 \text{ eq}}{1 \text{ mol HAc}} = 0.15 \text{ N}$$

**2-66.** Find the pH of a solution contain 10<sup>-3</sup> moles/L of hydrogen sulfide (H<sub>2</sub>S). pK<sub>a</sub> = 7.1

**Answer:**

$$C_{\text{TOT}} = 10^{-3} \text{ H}_2\text{S}$$

$$\text{pK}_a = 7.1$$

$$K_{a1} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] = 10^{-7.1}$$

$$\text{Electronegativity: } [\text{H}^+] = [\text{OH}^-] + [\text{HS}^-] \text{ assume } [\text{OH}^-] \ll [\text{HS}^-]$$

$$C_{\text{TOT}} = 10^{-3} = [\text{H}_2\text{S}] + [\text{HS}^-]$$

Substitute

$$K_{a1} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] = K_{a1} = [\text{HS}^-][\text{HS}^-]/C_T - [\text{HS}^-]$$

$$K_{a1} C_T - K_{a1} [\text{HS}^-] = [\text{HS}^-]^2$$

$$[\text{HS}^-]^2 + K_a [\text{HS}^-] - K_a C_T = 0$$

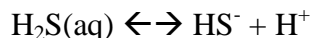
Using quadratic equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 - 4K_a C_T}}{2}$$

$$X = [\text{HS}^-] = [\text{H}^+] = 1.54 \times 10^{-5} = 10^{-4.8}$$

$$\text{pH} = 4.8$$

**2-67.** The Henry's Law constant for H<sub>2</sub>S is 0.1 mole/L-atm, and



Where K<sub>a</sub> = 10<sup>-7</sup>. If you bubble pure H<sub>2</sub>S gas into a beaker of water, what is the concentration of HS<sup>-</sup> if the pH is controlled and remains at 5.

a. moles/L

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**Answer:**

Step 1: Use Henry's Law to find the total dissolved sulfur species pure gas.

$$[H_2S_{(g)}] = 1 \text{ atm}$$

$$C_{H_2S \text{ tot}} = K_H C_g$$

$$= \left(0.1 \frac{\text{mol/L}}{\text{atm}}\right) (1 \text{ atm})$$

$$= 0.1 \frac{\text{mol}}{\text{L}}$$

Step 2: Use equilibrium constant

$$K_a = 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{[10^{-5}][HS^-]}{0.1}$$

$$10^{-8} = 10^{-5} [HS^-]$$

$$[HS^-] = 10^{-3} \frac{\text{mol}}{\text{L}}$$

b. mg/L, and

**Answer:**

$$C_{HS^-} \left(\frac{\text{mg}}{\text{L}}\right) = \left(10^{-3} \frac{\text{mol}}{\text{L}}\right) \left(\frac{32 \text{ g}}{\text{mol}}\right) \left(\frac{1000 \text{ mg}}{\text{g}}\right)$$

$$= 32 \frac{\text{mg}}{\text{L}}$$

c. ppm<sub>m</sub>?

$$C_{HS^-} = 32 \text{ ppm}_m$$

**2-68.** What is the pH of a solution containing  $1 \times 10^{-6}$  mg/L of OH<sup>-</sup> (25°C)?

**Answer:**

$$\text{pOH} = 6$$

$$\text{pH} = 14 - \text{pOH} = 8$$

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**2-69.** Find the hydrogen ion concentration and the hydroxide ion concentration in baking soda solution with a pH of 8.5.

**Answer:**

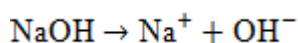
$$\begin{aligned} \text{pH} &= 8.5 \\ [\text{H}^+] &= 10^{-8.5} \\ \text{pOH} &= 14 - \text{pH} \\ [\text{OH}^-] &= 10^{-5.5} \end{aligned}$$

**2-70.** If 40 grams of the strong base, NaOH, are added to 1 liter of distilled water, what would the pH of the solution be, if

- Activity effects are neglected

**Answer:**

$$\frac{40 \text{ grams}}{\text{liter}} \times \frac{\text{mol}}{40 \text{ g}} = 1 \frac{\text{mol}}{\text{L}} \text{NaOH}_{(s)} = 1 \frac{\text{mol}}{\text{L}} \text{OH}^-$$



$$\text{pOH} = 0$$

$$\text{pH} = 14 - \text{pOH} = 14$$

- Activity effects are estimated using the Debye-Huckel approximation.

**Answer:**

$$\gamma_1 = 10^{-0.51 z^2 I^{0.5}} = 10^{-0.51(1)^2(1)^{0.5}} = 10^{-0.51}$$

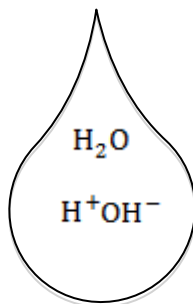
$$\gamma = 0.31$$

**2-71.** Write a complete mathematical model for a closed system consisting of water only at equilibrium. Be sure to include starting materials, a specie list, equilibria expressions, mass balances, a charge balance, and other constraints. Assuming activity effects are negligible, how do  $[\text{H}^+]$  and  $[\text{OH}^-]$  compare?

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**Answer:**

Species List & Diagram:

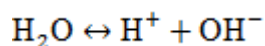


Equilibrium:

$$K_w = 10^{-14} = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-]$$

Note  $[H_2O] = 1$  from the activity definition.

Equation:

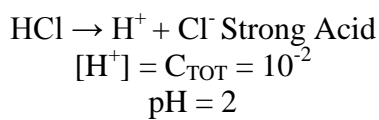


Mass Balance  $C_{H_2O_{tot}} = [H^+] + [OH^-]$

Charge Balance:  $[H^+] = [OH^-]$

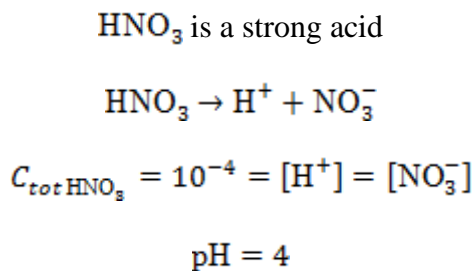
**2-72.** Estimate the pH of a solution containing  $10^{-2}$  M of HCl.

**Answer:**



**2-73.** Estimate the pH of a solution containing  $10^{-4}$  M of  $HNO_3$ .

**Answer:**

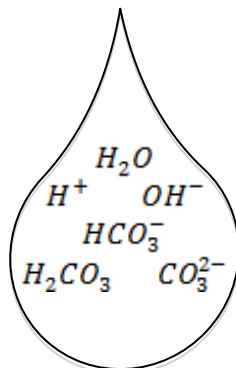


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2-74. Use a graphical approach to estimate the pH of a solution containing  $10^{-2}$  M of  $H_2CO_3$ .

**Answer:**

Step 1: Identify species in the solution



$$C_{TOT} = 10^{-2} \frac{\text{mol}}{L} \text{ of } H_2CO_3$$

Step 2: Identify relevant equations

$$\text{Mass Balance: } C_{TOT} = 10^{-2} \frac{\text{mol}}{L} = H_2CO_3 + HCO_3^- + CO_3^{2-}$$

$$\text{Equilibrium: } K_w = 10^{-14} = [H^+][OH^-]$$

$$K_{a1} = 10^{-6.3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$K_{a2} = 10^{-10.3} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$\text{Electroneutrality: } \sum \text{cations} = \sum \text{anions}$$

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Step 7: Check Solution

*from electroneutrality*

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

$$10^{-4.2} \cong 10^{-9.8} + 10^{-4.2} + 2(10^{-10.9})$$

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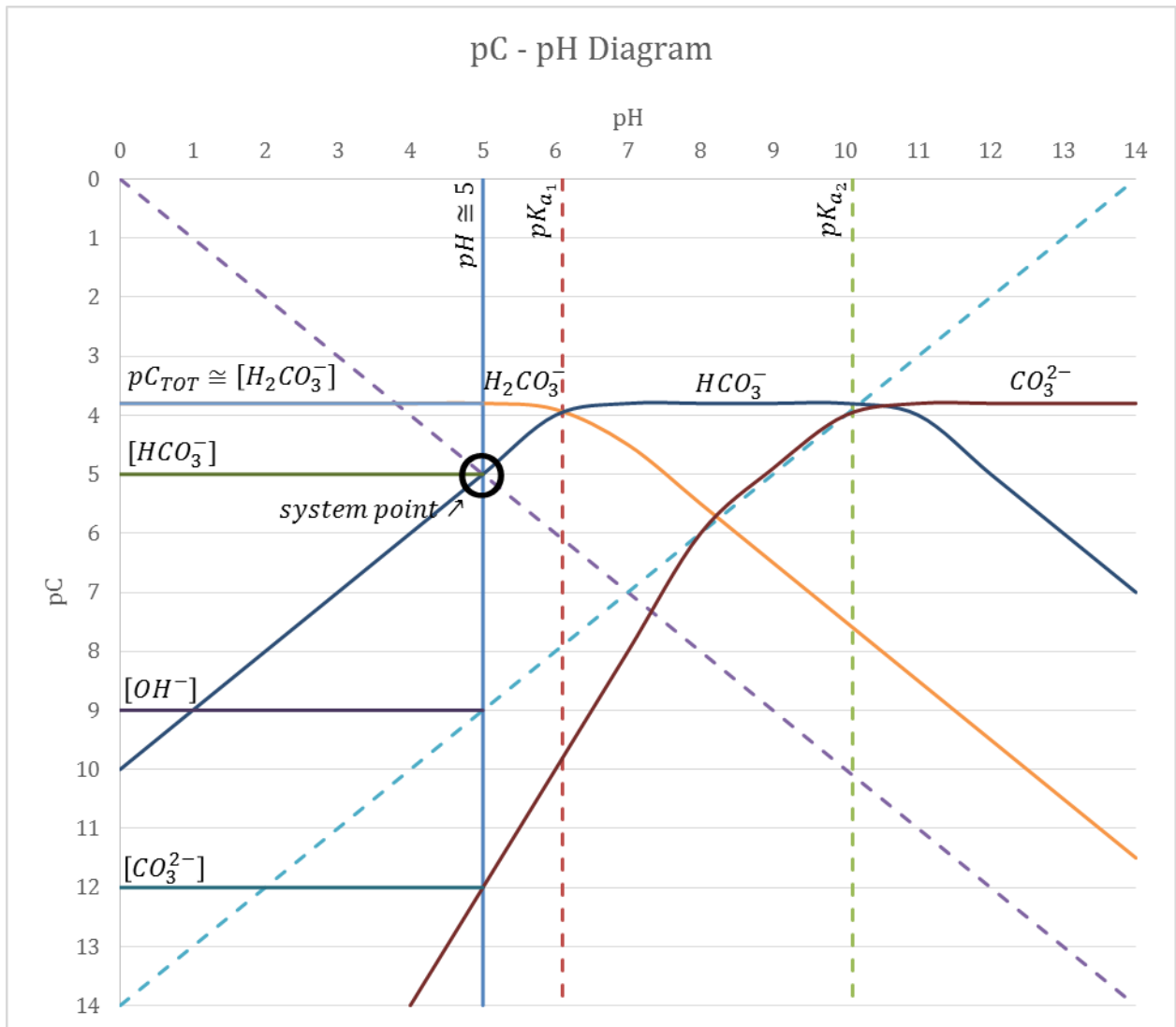
$$C_{H_2CO_3} = C_{TOT} - C_{HCO_3^-} = 10^{-2} - 10^{-4.2} \cong 10^{-2}$$

$$\text{Thus } [H_2CO_3] = 10^{-2}$$

$$[HCO_3^-] = [H^+] = 10^{-4.2}$$

$$[OH^-] = 10^{-9.8}$$

$$[CO_3^{2-}] = 10^{-10.9}$$



**2-75.** Use a graphical approach to estimate the pH of pristine rainfall of the early Earth if the acidity were due solely to atmospheric  $CO_2$  concentrations of 2,240 ppm<sub>v</sub>.



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**Answer:**

$$CO_{2(g)} = 2,240 \text{ ppm}_v = \frac{2,240 \text{ atm } CO_2}{10^6 \text{ atm air}} = 0.00224 \text{ atm}$$

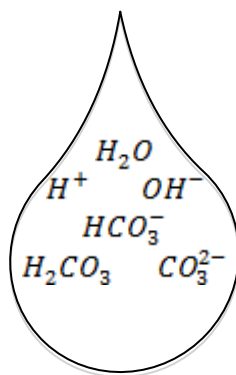
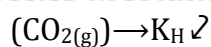
$$\text{from Henry's Law, } K_H = 0.033363 \frac{\text{mol/L}}{\text{atm}}$$

(see table 2.3)

$$C_{TOT} = (0.00224 \text{ atm})(0.033363 \frac{\text{mol/L}}{\text{atm}}) = 7.5 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$pC_{TOT} = -\log(7.5 \times 10^{-5} \text{ mol/L}) = 4.13$$

*The species in solution are:*



*The equilibrium equations are*

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$K_{a_1} = \frac{[H^+][OH^-]}{[H_2CO_3]} = 10^{-6.3}$$

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

*The mass balance equation is*

$$C_{TOT} = 10^{-3.6} \frac{\text{mol}}{\text{L}} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

*The electroneutrality equation is*

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

*CO<sub>2</sub> acts as an acid when dissolved in solution,*

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so lets assume the basic compounds  
 $[OH^-]$  and  $[CO_3^{2-}]$  are small.

The system point will occur at

$$[H^+] = [HCO_3^-]$$

This occurs where the  $[H^+]$  line crosses the  $[HCO_3^-]$  line, at  $pC = pH = 5.2$

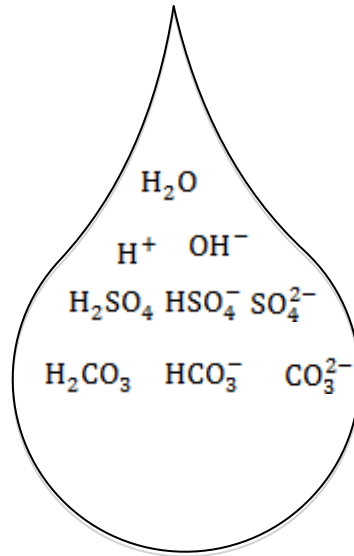
Thus  $[H^+] = [HCO_3^-] = 5.9 \times 10^{-6} \text{ mol/L}$

**2-76.** Acid rainfall due to sulfur emission leads to the addition of  $10^{-4} \text{ M}$  of  $H_2SO_4$  in rainfall over the northeastern United States during the 1970s and 80s. Carbon dioxide levels at that time were approximately 375 ppm<sub>v</sub>.

- Use the graphical approach to show the pH of rainfall over the northeastern United States during that time period.
- Also, estimate the concentration of carbonic acid and bicarbonate ion in the rainfall.

**Answer:**

Draw species list:



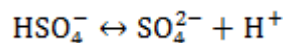
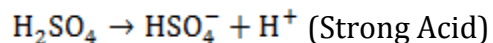
Aqueous concentrations:

$$\begin{aligned}
 C_{H_2CO_3^*} &= K_H P_{CO_2} = \left(0.033363 \frac{\text{mol}}{\text{L-atm}}\right) (375 \times 10^{-6} \text{ atm}) \\
 &= 1.25 \times 10^{-5} \frac{\text{mol}}{\text{L}} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]
 \end{aligned}$$

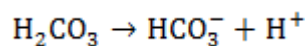
$$C_{H_2CO_3^*} = 10^{-4} \frac{\text{mol}}{\text{L}} = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$$

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Equilibrium Constants:



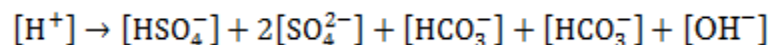
$$K_{a_2} = 10^{-1.99} = \frac{[\text{SO}_4^{2-}][\text{H}^+]}{[\text{HSO}_4^-]}$$



$$K_{a_1} = 10^{-6.37} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

$$K_{a_2} = 10^{-10.33} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

Charge Balance Equation:



Where  $\text{HSO}_4^-$  does not cross  $\text{H}^+$  line at concentration.

Both of the  $\text{HCO}_3^-$  are potentially small due to their lower concentration and acidity.

$\text{OH}^-$  is small due to its relationship with  $[\text{H}^+]$ .

Therefore, examine  $[\text{H}^+] = 2[\text{SO}_4^{2-}]$  as a system point.

From graphical analysis at  $[\text{H}^+] = 2[\text{SO}_4^{2-}] \cong 2(10^{-4}) = 10^{-3.7}$

(a)  $\text{pH} = 3.7$

(b) It follows then that the concentration of each ion is approximately:

$$\begin{aligned}[\text{SO}_4^{2-}] &= 10^{-4} \\[\text{H}_2\text{CO}_3] &= 1.25 \times 10^{-5} \\[\text{HSO}_4^-] &\cong 10^{-6} \\[\text{HCO}_3^-] &\cong 10^{-7.8} \\[\text{OH}^-] &\cong 10^{-10.3} \\[\text{CO}_3^{2-}] &\cong 10^{-13.3}\end{aligned}$$

**2-77.** Calculate the solubility of magnesium carbonate,  $\text{MgCO}_3$ , at  $25^\circ\text{C}$  in distilled water? Assume the solution acts as an ideal-fluid. The solubility product constant is  $K_{\text{sp}} = 4 \times 10^{-5}$ .

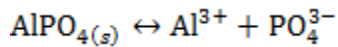
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**Answer:**

$$\begin{aligned}K_{sp} &= 4 \times 10^{-5} = \{Mg^{2+}\}\{CO_3^{2-}\} / \{MgCO_3\}_s = [Mg^{2+}][CO_3^{2-}] \\[Mg^{2+}][CO_3^{2-}] &= S \\S &= 4 \times 10^{-5} \\S &= 8 \times 10^{-2} \\[Mg^{2+}] &= [CO_3^{2-}] = 0.06 \text{ mol/L}\end{aligned}$$

**2-78.** Calculate the solubility of aluminum phosphate,  $AlPO_4$ , at  $25^\circ C$  in distilled water? Assume the solution acts as an ideal-fluid. The solubility product constant is  $k_{sp} = 3.2 \times 10^{-23}$ .

**Answer:**



$$K_{sp} = [Al^{3+}][PO_4^{3-}] = 3.2 \times 10^{-23}$$

$$\text{Let } [Al^{3+}] = S = [PO_4^{3-}]$$

$$\text{Then } S^2 = 3.2 \times 10^{-23}$$

$$S = (3.2 \times 10^{-23})^{0.5} = 5.66 \times 10^{-12}$$

$$[Al^{3+}] = [PO_4^{3-}] = 5.66 \times 10^{-12} \frac{\text{mol}}{\text{L}}$$

$$\log(K_{oc})_K = 1.00 \log(K_{ow}) - 0.21$$

$$\log(K_{oc})_K = \log(700) - 0.21$$

$$K_{ocK} = 4.32$$

$$\log(K_{oc})_{sw} = 0.72 \log(K_{ow}) = 0.49$$

$$K_{ocsw} = 346$$

$$K_p = f_{oc} K_{oc} \Rightarrow K_{pk} = (0.06)432 = 26$$

$$K_{p_{sw}} = (0.06)346 = 20.7$$

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$$C_{aq} \approx \frac{C_{soil}}{K_p} = \frac{\left(0.01 \frac{\text{mg}}{\text{kg}}\right)}{26} = 0.00038 \frac{\text{mg}}{\text{L}}$$

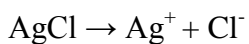
$$C_{aq} \approx \frac{C_{soil}}{K_p} = \frac{\left(0.01 \frac{\text{mg}}{\text{kg}}\right)}{220.76} = 0.00048 \frac{\text{mg}}{\text{L}}$$

The likely concentration of chlorobenzene in water is in the range of:

$$0.00038 < C_{aq} \left(\frac{\text{mg}}{\text{L}}\right) < 0.00048$$

**2-79.** Calculate the solubility of silver chloride, AgCl, at 25°C if the water already contains 10 mg/L of the chloride ion? Assume the solution acts as an ideal-fluid. The solubility product constant is  $K_{sp} = 3 \times 10^{-10}$ .

**Answer:**



$$K_{sp} = 3 \times 10^{-10} = \{\text{Ag}^+\} \{\text{Cl}^-\} / \{\text{AgCl}\}_s = [\text{Ag}^+][\text{Cl}^-]$$

The initial concentration of the chloride ion is:

$$[\text{Cl}^-]_i = \frac{10 \text{ mg}}{\text{L Cl}^-} \times \frac{\text{mmol}}{35 \text{ mg}} \times \frac{\text{mol}}{1000 \text{ mmol}} = 0.000286 \text{ mol/L}$$

Let  $[\text{Ag}^+] = S$  and  $[\text{Cl}^-] = S + 0.00286$

$$K_{sp} = S(S + 0.00286) \text{ or } S^2 + S(0.00286) - K_{sp} = 0$$

Has the form of the quadratic equation

$$a = 1, b = 0.00286, c = -3 \times 10^{-10}$$

$$S = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad S = 1.04 \times 10^{-6} \text{ mol/L}, [\text{Ag}^+] = 1.0 \times 10^{-6} \text{ mol/L}, [\text{Cl}^-] = 0.0029 \text{ mol/L}$$

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**2-80.** Vinyl chloride is a colorless odorless gas used in the production of PolyVinyl Chloride (PVC) plastics and in numerous industries. Vinyl chloride is also a known human carcinogen and the US EPA's Maximum Contaminant Level (MCL) in drinking water is 0.002 mg/L or 2 ppb. The vinyl chloride concentration in the soil outside of a plastic factory is 0.007 mg/kg, and the soil has a 15% organic content. Vinyl chloride (chloroethene) has a reported octanol-water coefficient equal to 4. Estimate the organic carbon normalized partition coefficient,  $K_{oc}$ , using the estimation procedures based upon equations 2.73 and 2.74 and the sediment/water partition coefficient. Use the sediment/water partition coefficient to predict the possible equilibrium concentration of vinyl chloride in the groundwater.

**Answer:**

$$\log(K_{OC}) = 1.00 \log(K_{OW}) - 0.21 \quad (2.73)$$

$$K_{OC} = 10^{0.392}$$

$$\log(K_{OC}) = 0.72 \log(K_{OW}) - 0.49 \quad (2.74)$$

$$K_{OC} = 10^{0.923}$$

$$K_{P1} = f_{OC} K_{OC1} = 0.15 \times 10^{0.392} = 0.37$$

$$K_{P2} = f_{OC} K_{OC2} = 0.15 \times 10^{0.923} = 1.26$$

$$C_{WATER1} = \frac{C_{SOIL}}{K_P} = \frac{0.007 \text{ mg/kg}}{0.37} = 0.02 \text{ mg/L}$$

$$C_{WATER2} = \frac{0.007 \text{ mg/kg}}{1.26} = 0.006 \text{ mg/L}$$

$0.006 < C_{WATER} < 0.02 \text{ mg/L}$  (both of which are greater than the allowable 0.002 mg/L MCL)

**2-81.** The US EPA's Maximum Contaminant Level (MCL) in drinking water is 0.005 mg/L or 5 ppb for carbon tetrachloride. The carbon tetrachloride concentration in the soil outside of a factory is 0.01 mg/kg, and the soil has a 1% organic content. carbon tetrachloride has a reported octanol-water coefficient equal to 400. Estimate the organic carbon normalized partition coefficient,  $K_{oc}$ , using the estimation procedures based upon equations 2.73 and 2.74 and the sediment/water partition coefficient. Use the sediment/water partition coefficient to predict the possible equilibrium concentration of carbon tetrachloride in the groundwater.

**Answer:**

$$\log(K_{OC}) = 1.00 \log(K_{OW}) - 0.21 \quad (2.73)$$

$$K_{OC} = 10^{2.39}$$

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$$\log(K_{OC}) = 0.72 \log(K_{OW}) - 0.49 \quad (2.74)$$

$$K_{OC} = 10^{2.36}$$

$$K_{P1} = f_{OC} K_{OC1} = 0.15 \times 10^{2.39} = 2.47$$

$$K_{P2} = f_{OC} K_{OC2} = 0.15 \times 10^{2.36} = 2.31$$

$$C_{water} = \frac{C_{SOIL}}{K_p} = \frac{0.01 \text{ mg/kg}}{2.47} = 0.0041 \text{ mg/L}$$

$$C_{WATER2} = \frac{0.01 \text{ mg/kg}}{2.31} = 0.0043 \text{ mg/L}$$

$$0.0041 < C_{water} < 0.0043 \frac{\text{mg}}{\text{L}}$$

*Less than MCL*

**2-82.** The US EPA's Maximum Contaminant Level (MCL) in drinking water is 0.1 mg/L or 100 ppb for chlorobenzene. The chlorobenzene concentration in the soil outside of a factory is 0.01 mg/kg, and the soil has a 6% organic content. Chlorobenzene has a reported octanol-water coefficient equal to 700. Estimate the organic carbon normalized partition coefficient,  $K_{OC}$ , using the estimation procedures based upon equations 2.73 and 2.74 and the sediment/water partition coefficient. Use the sediment/water partition coefficient to predict the possible equilibrium concentration of chlorobenzene in the groundwater.

**Answer:**

$$\log(K_{OC}) = 1.00 \log(K_{OW}) - 0.21 \quad (2.73)$$

$$K_{OC} = 10^{2.63}$$

$$\log(K_{OC}) = 0.72 \log(K_{OW}) - 0.49 \quad (2.74)$$

$$K_{OC} = 10^{2.54}$$

$$K_{P1} = f_{OC} K_{OC1} = 0.15 \times 10^{2.63} = 25.9$$

$$K_{P2} = f_{OC} K_{OC2} = 0.15 \times 10^{2.54} = 20.7$$

$$C_{water} = \frac{C_{SOIL}}{K_p} = \frac{0.01 \text{ mg/kg}}{25.9} = 0.00039 \text{ mg/L}$$

$$C_{WATER2} = \frac{0.01 \text{ mg/kg}}{20.7} = 0.00048 \text{ mg/L}$$

$$0.00039 < C_{WATER} < 0.00048 \frac{\text{mg}}{\text{L}}$$

*< than MCL*

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**2-83.** The US EPA's Maximum Contaminant Level (MCL) in drinking water is 0.002 mg/L or 2 ppb for Alachlor. The Arachlor 1221 concentration in the soil outside of a factory is 0.028 mg/kg, and the soil has a 12% organic content. Arachlor 121 has a reported octanol-water coefficient equal to 800. Estimate the organic carbon normalized partition coefficient,  $K_{OC}$ , using the estimation procedures based upon equations 2.73 and 2.74 and the sediment/water partition coefficient. Use the sediment/water partition coefficient to predict the possible equilibrium concentration of Arachlor 1221 in the groundwater.

**Answer:**

$$\log(K_{OC}) = 1.00 \log(K_{OW}) - 0.21 \quad (2.73)$$

$$K_{OC} = 10^{2.69}$$

$$\log(K_{OC}) = 0.72 \log(K_{OW}) - 0.49 \quad (2.74)$$

$$K_{OC} = 10^{2.58}$$

$$K_{P1} = f_{OC} K_{OC1} = 0.15 \times 10^{2.69} = 59.2$$

$$K_{P2} = f_{OC} K_{OC2} = 0.15 \times 10^{2.58} = 45.6$$

$$C_{water} = \frac{C_{SOIL}}{K_P} = \frac{0.028 \text{ mg/kg}}{59.2} = 0.00047 \text{ mg/L}$$

$$C_{WATER2} = \frac{0.028 \text{ mg/kg}}{45.6} = 0.00061 \text{ mg/L}$$

$$0.0005 < C_{WATER} < 0.0006 \frac{\text{mg}}{\text{L}}$$

$$C_{water} > MCL$$