Water Chemistry 1

Some Fundamentals
Water Quality Standards
Expressing Concentration (units)
pH
Water Sampling Programs

ATOMIC STRUCTURE

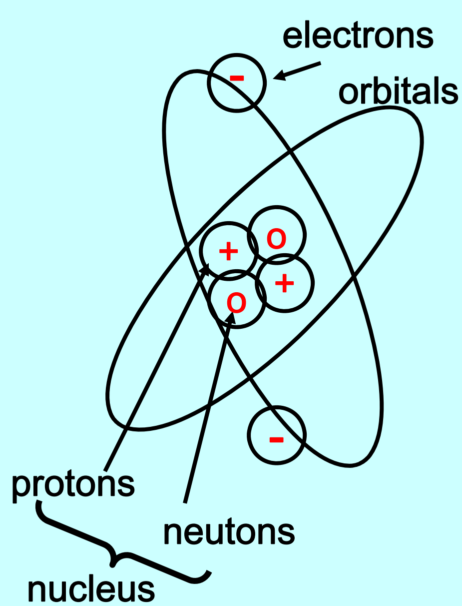
Each atom of an element is composed of a nucleus surrounded by electrons in various orbitals

Nucleus - a central concentration of mass consisting of protons and neutrons

Electrons - negatively charged particles of relatively low mass

Protons - positively charged particles of relatively high mass

Neutrons - particles with no charge but mass similar to that of protons



IONS (atoms with more or less electrons)

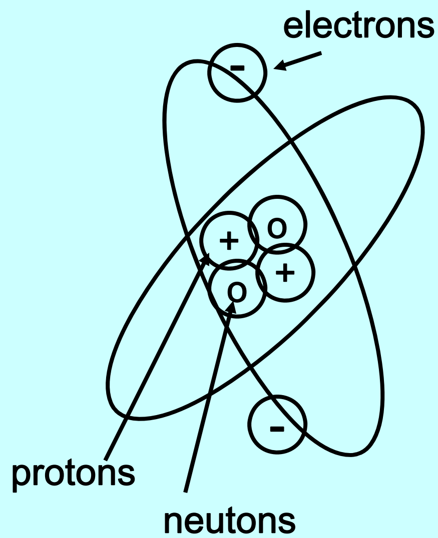
One more electron thar
\# protons results in a
negative charge

— ANION

One less electron than
\# protons results in a
positive charge

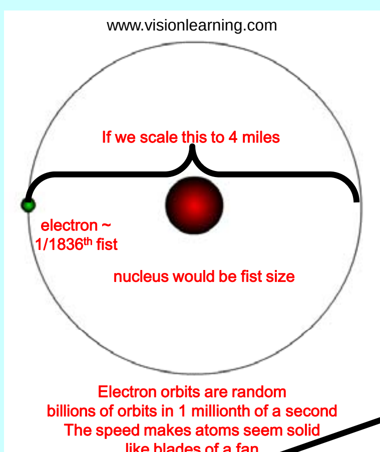
CATION

\+



Hydrogen

electrons (●), protons (●), and neutrons (●)



1 electron in first shell — 1

1 — atomic number = # protons

H

Hydrogen

1.008 (atomic weight)

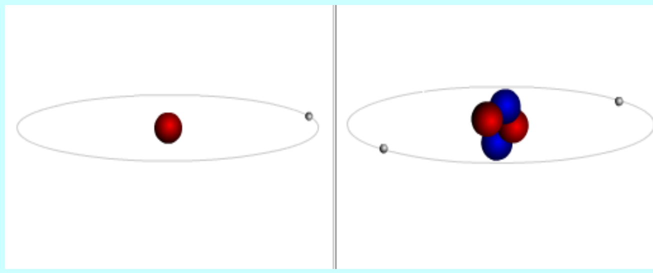
~ 1g H contains ~6.023×10^{23} atoms 602,300,000,000,000,000,000,000
Avagadro's #

Atomic Structures

electrons ( ), protons ( ) and neutrons ( )

Hydrogen
z = 1, mass = 1

Helium
z = 2, mass = 4



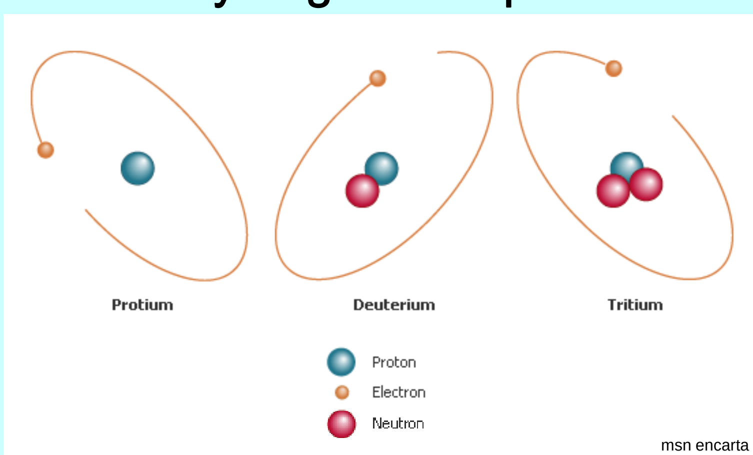
Elements are distinguished by their # of protons

# of neutrons and electrons can vary

Atomic mass ~ #protons + #neutrons

~ 4g He contains 6.023×10^{23} atoms 602,300,000,000,000,000,000,000

Hydrogen Isotopes

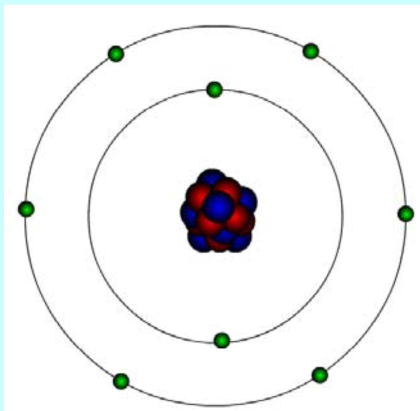


an atom with a DIFFERENT # OF NEUTRONS THAN PROTONS
is an ISOTOPE

isotopes have the SAME CHEMICAL BEHAVIOR BUT DIFFERENT MASS

Oxygen

electrons ( ), protons ( ), and neutrons ( )



8 (atomic number) 2 6

2 e^- 1st shell
6 e^- 2nd shell

O

Oxygen

15.999 (atomic weight)

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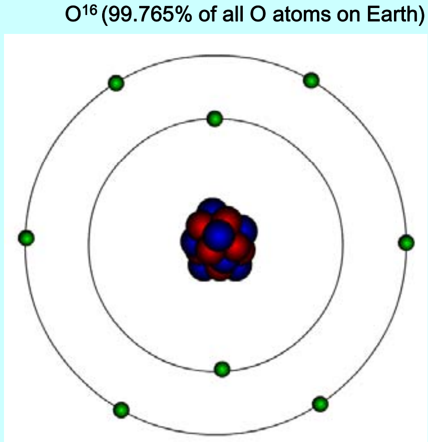
Bohr discovered electrons exist at discrete energy levels that we conceptualize as shells

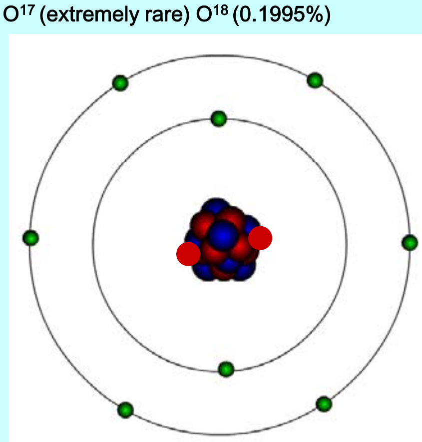
Maximum # electrons in shells increases outward : 2 8 18 32 50 72 98

~ 16g O contains 6.023×10^{23} atoms 602,300,000,000,000,000,000,000

Stable Oxygen Isotopes

O^{16} (99.765% of all O atoms on Earth) O^{17} (extremely rare) O^{18} (0.1995%)





O^{16}
99.765%
of all O atoms on Earth
8 neutrons

O^{18}
0.1995%

10 neutrons

H and O Isotopes Occur in Water

Ratios: $^{2}H/^{1}H$ and $^{18}O/^{16}O$

are expressed as units of parts per thousand (per mil)

deviation from Standard Mean Ocean Water

Heavier isotopes are left behind during evaporation

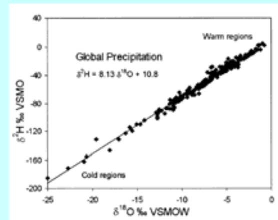
Heavier isotopes come out first during precipitation

(rainout effect – precipitation gets "lighter" across continent)

Global Meteoric Water Line (GMWL) $\delta D = 8\delta^{18}O + 10$

Is a benchmark relationship between D and ^{18}O

for evaluating waters from a given area

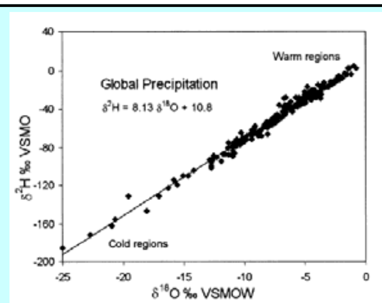


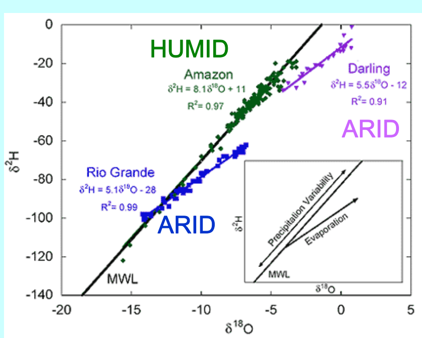
Local Meteoric Water Lines LMWL can be developed for an area using isotopic analysis of samples from local precipitation events

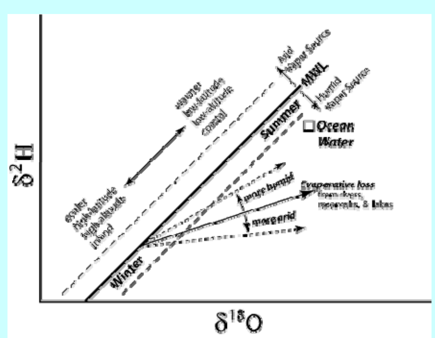
Comparing stable isotope data for individual water samples to the GMWL or LMWL reflects processes

For example, the lighter isotopes escape more readily during evaporation so water enriched in the heavier isotopes than the MWL indicates more evaporation

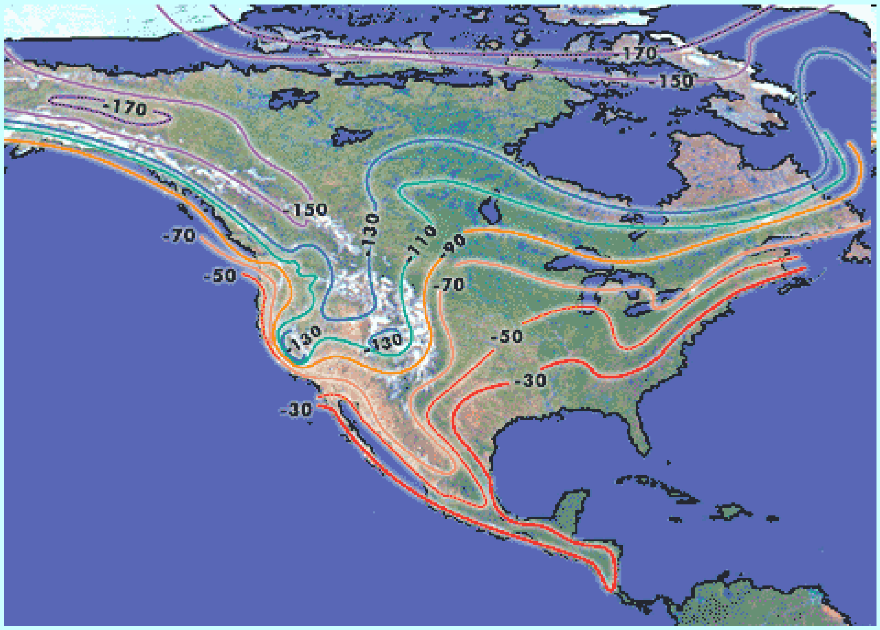
Differences in isotopic composition may be used to determine the source of water in the subsurface because fractionation ceases in the subsurface







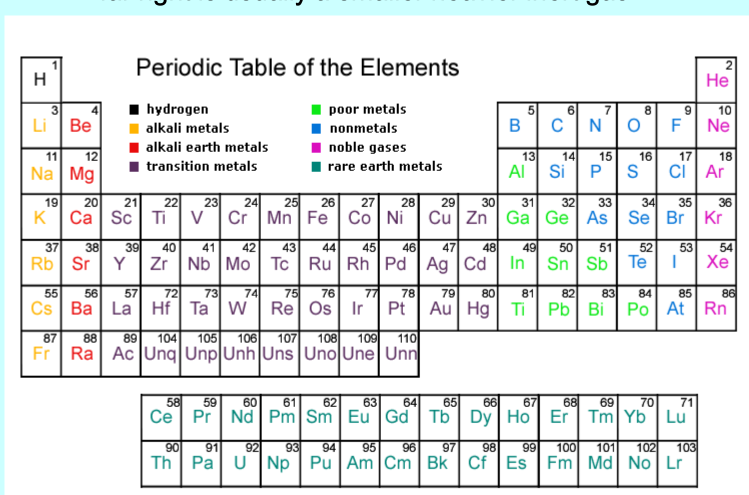
http://www.sahra.arizona.edu/programs/isotopes/oxygen.html



Average dD of precipitation in North America

Periodic Table

Columns = Groups - similar properties & same # electrons in outer shell
Rows = Periods - same number of shells
far left element is usually a larger lighter active solid
far right is usually a smaller heavier inert gas

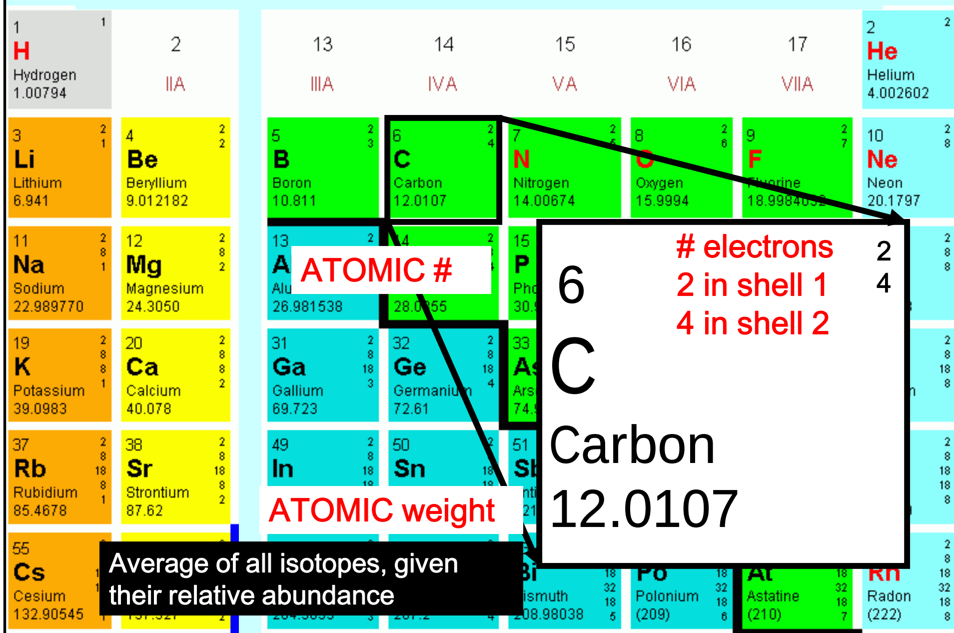


Periodic Table of the Elements

- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
- rare earth metals

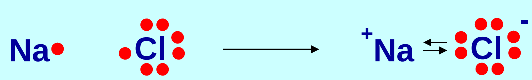
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

In each box



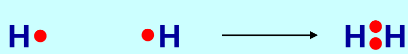
CHEMICAL BONDING

Ionic bonds - electrostatic attraction – one element transfers an outer e⁻ to another with an available slot in its outer shell



An electron is transferred

Covalent bonds - sharing of electrons

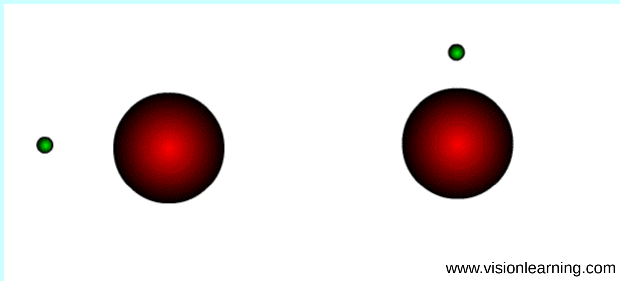


An electron is shared

Covalent Bonds

Covalent bonds form when atoms have a similar tendency to gain electrons

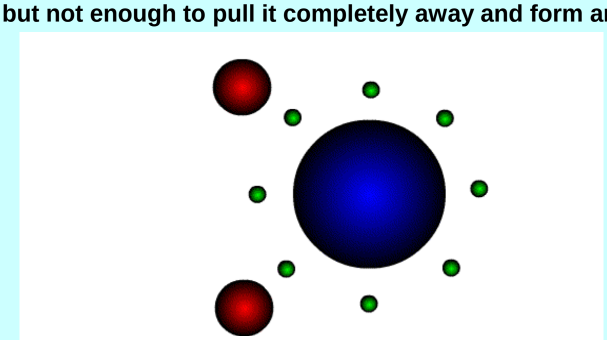
Covalent bonding between hydrogen atoms is <u>Nonpolar</u>
Because they have an equal affinity for the electron



H• + •H → H:H

Polar Covalent Bonds

Covalent bonding between hydrogen and oxygen atoms is <u>polar</u>
O has a stronger affinity for the e
but not enough to pull it completely away and form an ion



H• + :Ö: + •H → H:Ö:H

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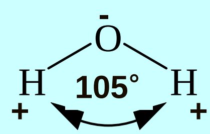
O needs 2 electrons to complete its outer shell --- Each H has 1
O shares one e^- from each of two H
In return it shares 2 e's with both H
Difference between the H-O bond in water & the H-H bond is the degree of sharing
Large O = stronger affinity for e than the small H's, so e's <u>spend more time</u> near O

WHY DO WE CARE IF A BOND IS IONIC OR COVALENT?

Physical & chemical properties of a compound depend on the character of the bonds

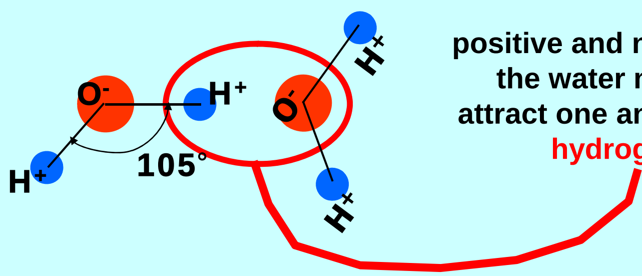
Of great importance is the SOLUBILITY of many constituents in water

Water is a POLAR COVALENT SOLVENT



A general rule is "like dissolves like"
Water dissolves ionic solids (e.g., NaCl, K_2SO_4) very well
Water is known as the "universal solvent"
but water is a poor solvent for nonpolar compounds
for example, organic compounds like benzene (C_6H_6)

ANOMALOUS PROPERTIES OF WATER



positive and negative ends of the water molecule can attract one another to form a hydrogen bond

hydrogen bonding causes water to have anomalous properties

high boiling & melting point - only natural substance found in all three states -- liquid, solid, gas at typical temperatures on Earth

maximum density at 4C (so ice floats!)

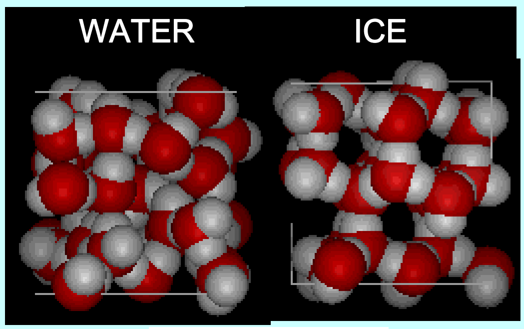
high specific heat index
absorbs a lot of heat before getting hot (a good thermal moderator)

high surface tension – moves with dissolved substances through the roots of plants and tiny blood vessels in our bodies

Water as Liquid and Solid

Liquid water is a partially ordered structure
strong H bonds are constantly formed and broken
Each molecule is
hydrogen-bonded to approximately 3.4 other water molecules

Solid water – Ice – is a rigid structure
Each molecule is hydrogen-bonded to 4 other water molecules
The regular structure holds the H2O molecules further apart



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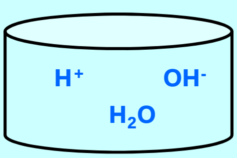
WATER AS A SOLVENT

Solvent
water



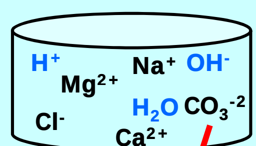
+

Solutes
cations & anions

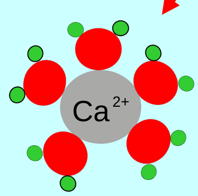
Crustal minerals are mostly +and- ions (e.g. Ca^{2+}, Mg^{2+}, CO_3^{2-}, Na^+, Cl^-) held by ionic bonds. When water molecules surround the ions they move from the crystal latice to become dissolved ions.

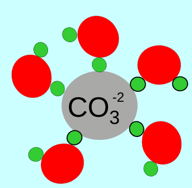
→

Solution
solvent + solutes



Ions are hydrated (surrounded by water dipoles) in solution, isolating them from their neighbors and neutralizing attractive forces that hold minerals together





UNITS OF EXPRESSION

we use various units of concentration

Mass Concentration

mass/mass units – ppm, ppb

mass/volume units – mg/L, g/L

$$1\,\text{ppm}\,(\text{parts per million}) = \frac{1\text{g}}{10^6\text{g}}\,\frac{10^3\text{mg}}{1\text{g}}\,\frac{10^3\text{g}}{1\text{kg}} = \frac{1\text{mg}}{1\text{kg}} = 1000\text{ppb}\,(\text{parts per billion})$$

$$C\ ppm = C\frac{\text{mg}}{\text{kg}} \qquad \text{fresh water density} \sim \frac{1\text{kg}}{1\text{L}} \quad \text{so } C\frac{\text{mg}}{\text{kg}}\,\frac{1\text{kg}}{1\text{L}} \sim C\frac{\text{mg}}{\text{L}}$$

Because the density of many natural waters is ~ 1 kg/L it is often sufficient to assume that mg/L and ppm are the same value

$$1\,\text{ppm}\,(\text{parts per million}) = \frac{1\text{g}}{10^6\text{g}} = \frac{1\text{mg}}{1\text{kg}} = \frac{1\text{mg}}{\text{L}}\ (\text{in most natural waters})$$

UNITS OF EXPRESSION

However we must use *Molar Concentration* for almost all geochemical calculations

Moles (1 mole = 6.023 x 10^{23} atoms or molecules)

$$\text{Molality (m)} = \frac{\text{moles of solutes, mol}}{\text{mass of solvent, kg}}$$

by weight solvent
L

$$\text{Molarity (M)} = \frac{\text{moles of solutes, mol}}{\text{volume of solution, L}}$$

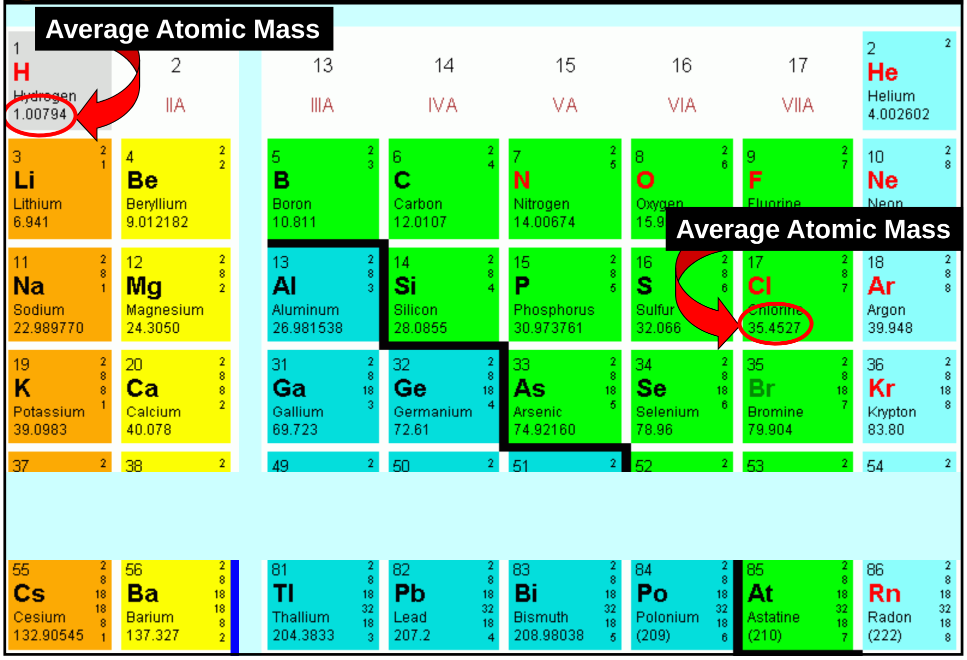
by volume solution
R

Molarity is the most common concentration unit involved in calculations dealing with volumetric stoichiometry

Conversion from mol/L (M) to mg/L:

$$\frac{\text{mol}}{\text{L}} \quad \text{molar mass in}\ \frac{\text{g}}{\text{mol}} \quad \frac{1000\ \text{mg}}{\text{g}} \quad = \quad \frac{\text{mg}}{\text{L}}$$

What is the molar mass for 1 mole of Hydrochloric Acid (HCl)?



UNITS OF EXPRESSION

Mole fraction (X) - **another form of molar concentration**

$$X_{\text{Solute}} = \frac{\text{moles of solute}}{\text{total moles of all components}}$$

the *mole fraction (X)* is typically used for solid solutions
solid solution between $KAlSi_3O_8$ and $NaAlSi_3O_8$
the mole fraction of $KAlSi_3O_8$ would be written as:

$$X_{KAlSi_3O_8} = \frac{\text{moles } KAlSi_3O_8}{\text{moles } KAlSi_3O_8 + \text{moles } NaAlSi_3O_8}$$

Percentage (%) - **the ratio of a solute to the solution**
If a solution concentration is given as a percentage, you can assume it is a mass percentage unless otherwise stated

Suppose you are given a concentrated solution of HCl labeled as 37.0% HCl, with a solution density of 1.19 g/mL
What is the Molarity of HCl?

UNITS OF EXPRESSION

Equivalents and Normality (N) - units : equivalents/liter

Equivalents (eq) are similar to moles, but take into account the valence of an ion (i.e. # of reactive units)

0.002 mol L^{-1} of Ca^{2+} = 0.004 eq L^{-1} Ca^{2+}
0.001 mol L^{-1} of Na^{+} = 0.001 eq L^{-1} Na^{+}
0.003 mol L^{-1} Al^{3+} = 0.009 eq L^{-1} Al^{3+}

Normality (*N*) is another name for eq L^{-1}

Alkalinity and Hardness are important parameters that are expressed as eq L^{-1} or meq L^{-1} (more on these later)

Say a laboratory reports the concentration of Ca^{2+} in a water sample as 92 mg/L. What is the normality of Ca^{2+} ?

THE LAW OF MASS ACTION

indicates that a system strives to equilibrium

$A + B \leftrightarrow C + D$

At equilibrium both reactions happen simultaneously

$A + B \rightarrow C + D$

$A + B \leftarrow C + D$

A chemical reaction can be written as

$aA + bB \leftrightarrow cC + dD$

a b c d are molar amounts of compounds A B C D

In simple terms, at equilibrium

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \text{constant}$$

[X] represents the equilibrium molar concentration of X

K is the equilibrium constant

If one compound changes concentration others adjust to maintain K

For equilibrium evaluations the [ ] of a pure liquid or solid is defined as 1

HYDROGEN ION ACTIVITY (pH)

pH is a "master variable" controlling aqueous chemistry systems

Dissociation of Water **– when water ionizes, the following simplified relationship applies:**

$H_20 \leftrightarrow H^+ + OH^-$

water molecule ↔ hydrogen ion + hydroxide ion

The corresponding equilibrium expression for this reaction is

$$K = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

where K = equilibrium constant

[ ] = molar concentration

we assume $[H_2O]$ is unity and don't bother to include it explicitly in the equations, so:

$K_w = [H^+]\,[OH^-]$

where K_w = equilibrium constant for water

pH is negative log of activity of the Hydrogen ion = - log[H⁺]

HYDROGEN ION ACTIVITY (pH)

Positive ions in solution must be balanced by negative ions

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

$$K_w = [H^+]\,[OH^-]$$

and substituting $[H^+]$ for $[OH^-]$ $\qquad K_w = [H^+]^2$

Taking the negative logarithm

$$-\log\,[H^+] = -\tfrac{1}{2}\log K_w$$

Just as pH represents $-\log\,[H^+]$

it is convenient to use pK to represent $-\log K_w$

$$pH = -\log[H^+] = -\tfrac{1}{2}\log K_w = \tfrac{1}{2}\,pK_w$$

In dilute aqueous solution at 25ºC, $K_w = 10^{-14}$

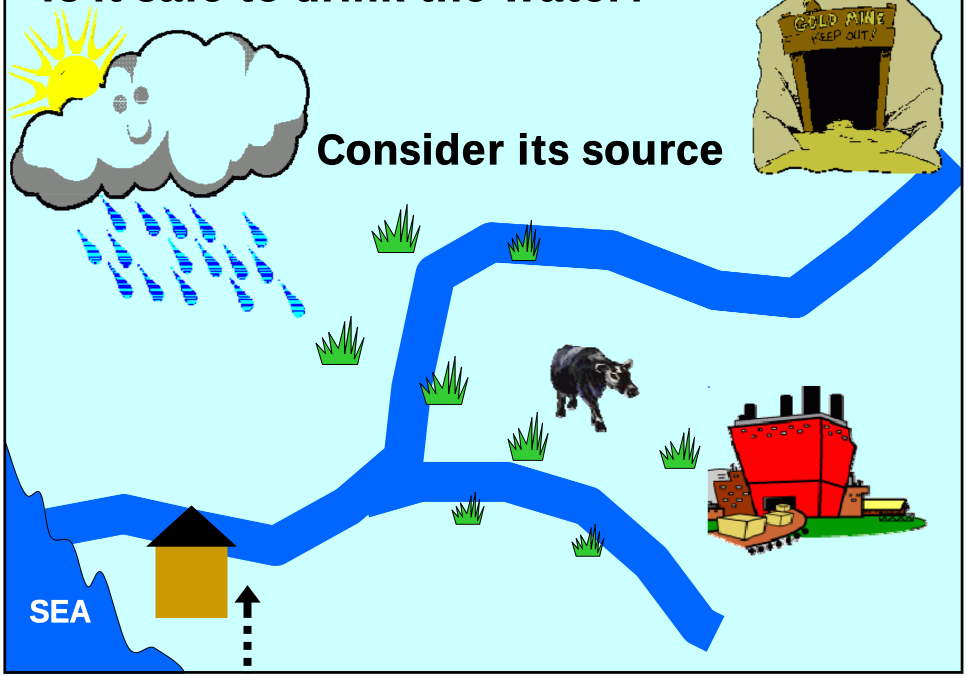
⇒ **the pH of pure water is 7.0**

Given the following ground water analysis:

Constituents	Conc.(ppm)
Na^+	145
Ca^{2+}	134
Mg^{2+}	44
HCO_3^-	412
SO_4^{2-}	429
Cl^-	34
TDS	1049.9
pH	5.5

Calculate the $[H^+]$ and $[OH^-]$ of the sample

Is it safe to drink the water?

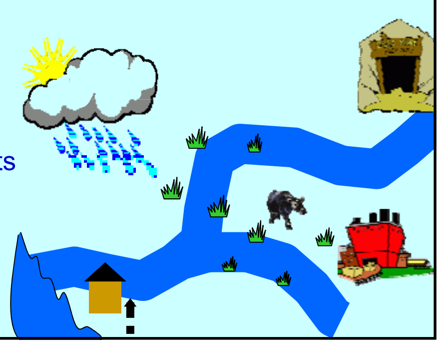


To evaluate the quality of the water and its source:
- Collect water samples
- Perform chemical analyses

To design a sampling program

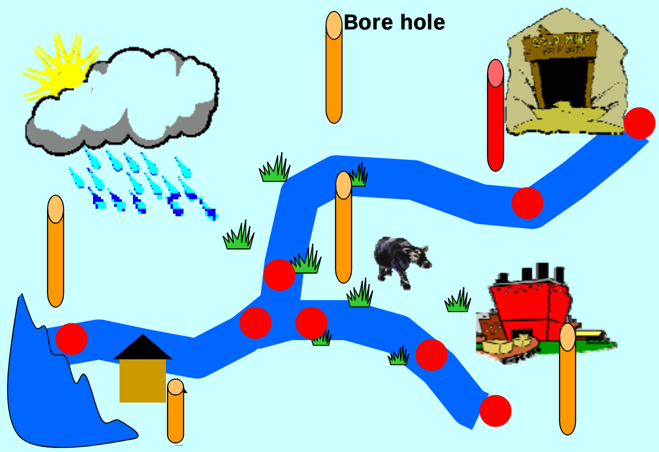
Determine the purpose
- define water chemistry, identify source of the water
- determine if the water meets drinking water standards
- determine source of contamination

Select sampling points
- Location
  - Sample Surface & Ground Water
  - Up and Down Gradient from potential sources of constituents
- Number
- Frequency



Determine if new wells are needed and select their location

Choose surface water sampling sites



Determine characteristics to analyze

Some measurements can or must be made On-site

For example:Temperature, pH, Eh, specific conductivity

For Lab analysis (Preserve: Filter, Chill, often Acidify)

Always check procedures before sampling http://water.usgs.gov/owq/FieldManual/

STABILIZE IONS BY PRESERVATION

to prevent alteration due to reactions

oxidation, reduction, precipitation, adsorption, and ion exchange

before analysis in a laboratory

REFRIGERATION minimizes chemical change due to biologic activity

ACID prevents precipitation of cations

General USGS procedures:

Analyses	Bottle type	Bottle cap	Treatment
Anions	Clear plastic	Black	FU
Cations	Clear plastic	Clear	FA
Nutrients	Brown plastic	Black	RC,FC
Trace elements	Clear plastic	Clear	FA
Organic compounds	Brown glass	Teflon lined	FC

F = filtered
U = untreated
A = nitric acid (HNO3)
R = raw (unfiltered)
C = chill & maintain to 4C

WATER ANALYSIS

Routine anaylsis typically includes the red items

Major Constituents (typically > 5mg/L)	Minor Constituents (typically 0.01-10mg/L)
Bicarbonate	Boron
Calcium	Carbonate
Chloride	Floride
Magnesium	Iron
Nitrogen	Oxygen
Silicon	Nitrate
Sodium	Potassium
Sulfate	Strontium
Carbonic acid	Bromide
	Carbon dioxide

Other
- Ion Balance
- pH
- Total Dissolved Solids
- Alkalinity **presence of $[HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+]$ more about this later**
- Hardness presence of multivalent ions **more about this later**

ANALYTICAL METHODS

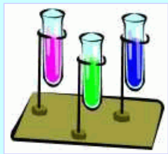
Inorganic Chemicals - *Ion Chromatography*
ICP-Mass Spectrometry
(for example: Arsenic, Barium, Calcium, Chloride, Fluoride, Lead, Magnesium, Mercury, Nitrate, Nitrite, Silica, Sodium)

Organic Chemicals - *Gas Chromatography*
(for example: Benzene, Carbon tetrachloride, Vinyl chloride, Xylenes, Tetrachloroethylene, Trichloroethylene, Toluene)

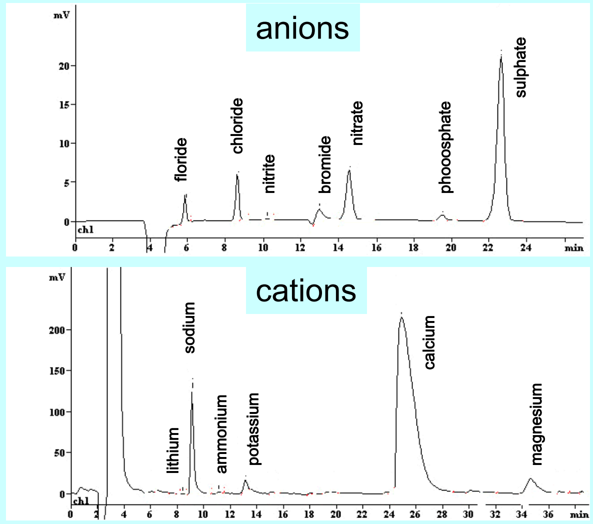
Microorganisms - *Membrane Filter Methods*
(for example: Coliforms, Viruses)

Radionuclides - *Radiochemical Methods*
(for example: Radium, Uranium, Radon)

Ion Chromatography



Chromatography: Atomized sample is carried through a column and constituents are delayed by different degrees due to their affinity for the material lining the column thus their signal arrives at different times



Glacial Water

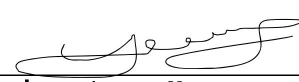
Image and data from Monica Bruckner
http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic.html

LABORATORY REPORT

Client: Eileen Poeter
Project: Analytical Lab Services
Date Collected: 10/08/08
Sample Identification: Well Water

Collected by: SS
Project Number: CLO00001
Time Collected: 9:35 am
Lab Number: 0 1 000

Analysis	Results	Units
Total Coliform Bacteria	50	#/100mL
Nitrate-Nitrogen	4.55	mg/1
pH	7.50	
Fluoride	5	mg/1
Hardness as CaCo3	280	mg/1
Sulfate Sulfur	32.0	mg/1
Chloride	25.4	ppm
Specific Conductance	344	μmhos/cm

Submitted by: 
Laboratory Manager

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- On the basis of the above test result(s), this water sample DOES NOT MEET EPA Drinking Water Standards.
- The following notes apply to this sample:
  - The Total Coliform Bacteria exceeded the maximum level of 1 colony/100mL.
  - The Fluoride level exceeded the limit of 4 mg/L.

Submitted by: ______________________
Laboratory Manager

Coliform bacteria are common in the environment and are generally not harmful

BUT may indicate contamination with animal or human waste that may be contaminated with germs that can cause short-term effects, such as diarrhea, cramps, nausea, headaches, or other symptoms, for example

Giardia lamblia

AND some may be fatal to those with weak immune systems

There are many strains of harmless E. coli, but one is particularly troublesome: E. coli O157:H7

Cryptosporidium

DRINKING WATER STANDARDS

http://www.epa.gov/safewater/mcl.html#mcls

Some examples of Primary Drinking Water Regulations

legally enforceable for public water systems (see link above for all items)

Item	MCLG Maximum Contaminant Level Goal	MCL Maximum Contaminant Level (considers technology & cost)
Nitrate	10 mg/L	10 mg/L
Total Coliform	zero	5% of samples/mo, 0 if < 40
Flouride	4 mg/L	4 mg/L
Arsenic	zero	0.01 mg/L

Examples of Secondary Drinking Water Regulations

non-enforceable guidelines on contaminants that may cause cosmetic or aesthetic effects (skin/tooth discoloration) or (taste, odor, or color)

see link above for all items

Item	**Standard**
pH	6.5-8.5
Total Dissolved Solids	500 mg/L
Chloride	250 mg/L

Fluoride Maximum Contaminant Level - 4mg/L

Reason for Monitoring	**Sources**	**Health Effects**
Drinking water standard Water quality standard Health risks	Natural deposits Fertilizer Aluminum industries Water additive (1mg/L US)	Skeletal and dental fluorosis



EXAMPLES of IMPURITIES in NATUAL WATER

Origin	Positive Ions	Negative Ions
Contact of water with minerals, soils, and rocks	Ca^{+2}, Fe^{+2} Mg^{+2}, Mn^{+2} K^{+}, Na^{+}, Zn^{+2}	HCO_3^{-}, CO_3^{-2} Cl^{-}, F^{-}, NO_3^{-} PO_4^{-3}, OH^{-}, SO_4^{-2} $H_2BO_3^{-}$
The atmosphere (rain)	H^{+}	HCO_3^{-}, Cl^{-}, SO_4^{-2}
Decomposition of organic matter in the environment	NH_4^{+}, H^{+}, Na^{+}	Cl^{-}, HCO_3^{-}, OH^{-}, NO_2^{-}, NO_3^{-}, HS^{-} Organic radicals
Municipal, industrial, and agricultural sources and other human activity	Inorganic ions, including a variety of heavy metals	Inorganic ions, organic molecules