

The Fundamentals of Water Chemistry

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A Mole

A Millimole

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Capacity Building and Institutional Cooperation in the field of Hydrogeology for Faryab Province , Afghanistan

NORPLAN

A question

A water sample contains

40 g/L calcium ions Ca^{++}
23 g/L sodium ions Na^{+}
1 g/L of hydrogen ions H^{+}

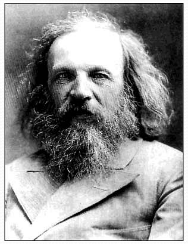
Which type of ion is most abundant?

Atomic mass units

Every atom and molecule has a mass

It is measured in atomic mass units

- 1 amu is approximately the mass of one hydrogen atom
- Carbon has a mass of 12 amu
- Oxygen has a mass of 16 amu
- Sodium has a mass of 23 amu
- Calcium has a mass of 40 amu
- Water (H_2O) has a mass of 18 amu



The Siberian scientist Dmitry Mendeleev (1834-1907) systematised this information

The periodic table of the elements

This particularly clear version is from Los Alamos National Laboratory
http://periodic.lanl.gov/index.shtml

Atomic number → 2
Atomic mass → 4.003

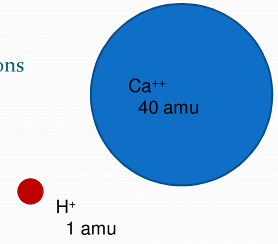
Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.79
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	*	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.38	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	**	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

The answer to our question

Calcium is 40 times heavier than hydrogen, so

40 g/L calcium is exactly the same number of ions as
23 g/L sodium ions Na^+
1 g/L of hydrogen ions H^+

In fact 40 g of calcium ions is 6×10^{23} ions
23 g of sodium ions is 6×10^{23} ions
1 g of hydrogen ions is 6×10^{23} ions



Moles and Millimoles

Moles
A Scaling Factor

A mole is simply a fixed (macroscopic) number of particles, namely 6×10^{23} particles per mole.

This is the number of particles in 1 g hydrogen atoms.

- Thus, 1 mole Na = 23 g
- 1 mole H_2O = 18 g

Conc. in mmol/l = conc. in mg/l / molar mass
[mmol/l]= [mg/l]/[molar mass g/mol]

Another question

Sodium nitrate is a salt with the formula $NaNO_3$
If Na = 23 atomic mass units, N = 14 amu and O = 16 amu
What is its molecular mass ?
What is the mass of 1 mole of $NaNO_3$?

If you dissolve 85 mg of sodium nitrate in 1 L of water
$NaNO_3 \Leftrightarrow Na^+ + NO_3^-$
What concentration of sodium ions and what concentration of nitrate ions do you get?

Equivalents

One mole of calcium ions reacts with one mole of sulphate to precipitate gypsum:

- $Ca^{++} + SO_4^{=} + 2H_2O \Leftrightarrow CaSO_4.2H_2O$

but, two moles of sodium react with one of sulphate to precipitate mirabilite

- $2Na^{+} + SO_4^{=} + 10H_2O \Leftrightarrow Na_2SO_4.10H_2O$

Thus, one mole of calcium is *equivalent in terms of charge* to two moles of sodium

Equivalents

1 equivalent = 1 mole of charge

Conc. in meq/l = conc. in mmol/l x charge

[meq/l] = [mmol/l].z = [mg/l].z/[molar mass g/mol]

Thus 10.02 mg/l Ca^{++} (Ca = 40.08 g/mol)
= 0.25 mmol/l
= 0.5 meq/l

11.5 mg/l Na^{+} (Na = 23 g/mol)
= 0.5 mmol/l
= 0.5 meq/l

Alkalinity

This is a *constructed* concept.

Alkalinity is

- the capacity of a solution to neutralise acids
- the total (in meq/l) of basic species in a solution

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

where [ ] = concentration in mmol/l

Alkalinity

Alkalinity is measured by a titration.

- A known volume of sample is taken and stirred with a magnetic stirrer. A pH electrode is inserted
- A strong acid (hydrochloric or sulphuric) is added drop by drop until the pH has dropped to a given value, often pH 4.3
- The amount of acid (meq) required to neutralise one litre of water is calculated.

Why pH 4.3 ?

$CO_3^{=} + 2H^+ \rightarrow HCO_3^- + H^+ \rightarrow H_2CO_3 = H_2O + CO_2$

pH 8.2 — pH 4.3

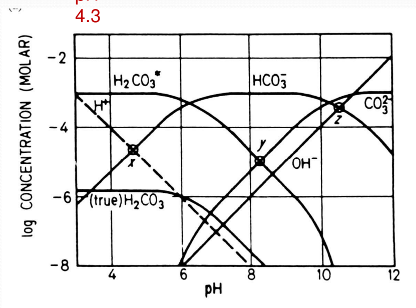
At pH 4.3, almost all HCO_3^- has been converted to carbonic acid.

Alkalinity is cited in meq/L

Old unit is mg/L $CaCO_3$

1 meq/L = c. 50 mg/L $CaCO_3$

1 meq/L = c. 61 mg/L HCO_3^-



After Stumm & Morgan 1996

pH

pH is a measure of the activity of hydronium (hydrogen) ions (protons) in solution

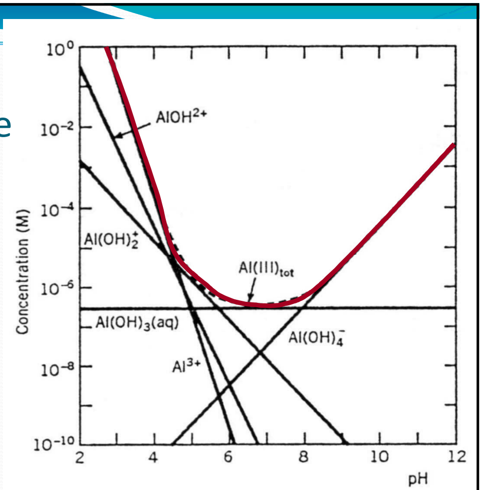
$pH = -\log_{10}(H^+)$

Thus, in water of pH=7, there are 10^{-7} mole/l hydrogen ions or 0.0001 mg/l.

In water of pH = 3, there are 10^{-3} mole/l hydrogen ions or 1 mg/l.

Why is pH a Master Variable ??

After Stumm & Morgan 1996



- It controls the solubility of elements, such as metals Al, Fe and Zn

Electrical conductivity (EC)
Total dissolved solids (TDS)

The more dissolved ions there are in water, the better it is at conducting electricity.

EC varies with temperature. We normally cite it at a standard temperature of either 20 or 25°C

Rule 1: 1 meq/L of cations (or 1 meq/L of anions)
results in 100 μS/cm of EC up to around 2000 μS/cm

Rule 2: TDS (mg/L) = EC (μS/cm) x f

- where f = 0.55 for a water dominated by sodium chloride
- f = 0.75 for a water dominated by calcium bicarbonate

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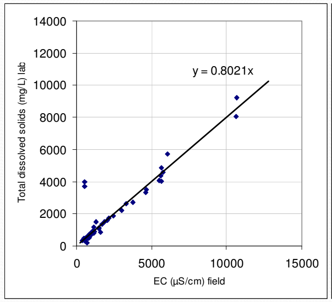
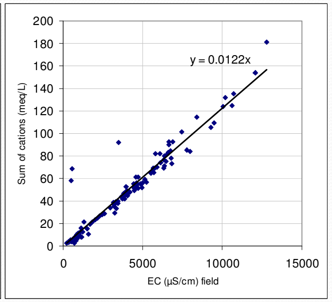
In fact, in Faryab





TDS = EC x 0.8

1 meq cations = 82 µS/cm of EC

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When you receive the results of an analysis from a laboratory, you should do some basic checks

- Are the laboratory's methods documented ?
- Have the analyses been calibrated or verified against known standards?
- What are the accuracy / precision of the laboratory's methods?
- Is there a large ion balance error?
- Are the results realistic?
- Are the units of measurement clearly documented

Ion Balance

Water is electrically neutral, thus:

Σ cations (meq/l) = Σ anions (meq/l)

$$\Sigma \text{cations} = \frac{2.[Ca^{++}]}{40.08} + \frac{[Na^{+}]}{22.99} + \frac{2[Mg^{++}]}{24.31} + \frac{[K^{+}]}{39.1}$$

where [ ] = conc. in mg/l

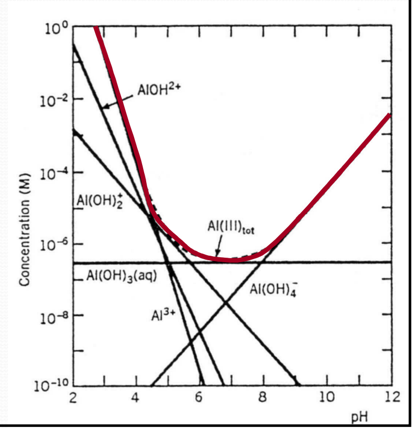
$$\Sigma \text{anions} = \frac{2.[SO_4^{=}]}{96.06} + [\text{alkalinity}] + \frac{[Cl^{-}]}{35.45} + \frac{[NO_3^{-}]}{62.0}$$

$$IBE = \frac{(\Sigma \text{cations} - \Sigma \text{anions})}{(\Sigma \text{cations} + \Sigma \text{anions})} \times 100\%$$

Solubility…is it realistic?

In most circum-neutral groundwaters, the concentration of dissolved aluminium should be very low.

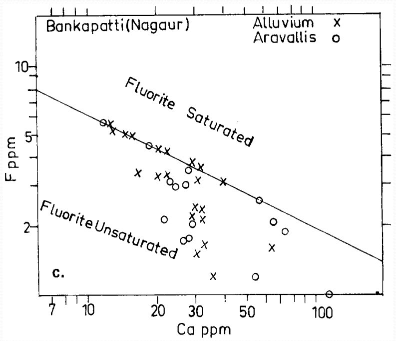
If not…particulate contamination??



Solubility…is it realistic?

The solubility of fluorite (CaF_2) often limits the solubility of fluoride.

Thus, high fluoride is usually found in low Ca waters



From Handa 1975. Geochemistry and genesis of fluoride-containing groundwaters in India

Some common mistakes!

Don't confuse mg/L with µg/L
1000 micrograms = 1 milligram!

Some labs cite nitrate as NO_3^-
Other labs cite it as nitrate-nitrogen (NO_3^--N)
Remember that 50 mg/L NO_3^- is c. 11 mg/L (NO_3^--N)

Be careful how laboratories cite alkalinity or bicarbonate
Is it really bicarbonate (HCO_3^-)
Or is it total alkalinity in meq/L or mg/L $CaCO_3$ equivalent