Updated: 24 January 2020

Print version

CEE 680: Water Chemistry

Lecture #3

Intro: Atoms and Isotopes

(Stumm & Morgan, Chapt. 4.9)

(Pg. 195-202)

Best source for stable isotopes is:

Eby, Chapter 6, especially pg. 181-186

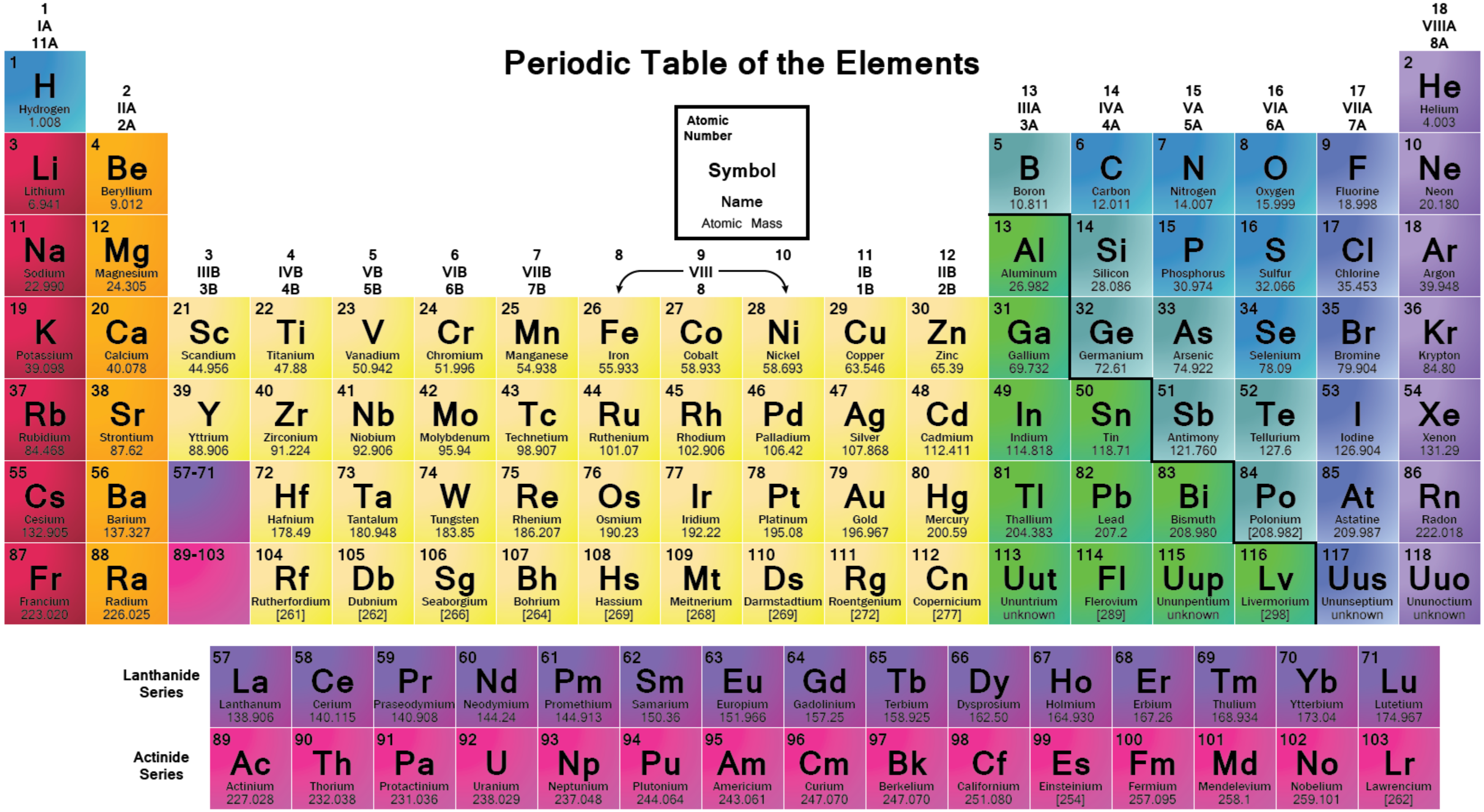
Molarity

- One mole of any substance contains 6.02 x 10^{23} (Avogadro's number) elementary chemical units (e.g., molecules).
- It is very convenient to measure concentrations in moles, since reactions conform to the law of definite proportions where integer ratios of reactants are consumed (e.g., 1:1, 1:2, etc.) on both a molecular and molar basis.
- It is calculated by:

$$Molarity = \frac{mass/L}{GFW}$$

- Often use M, mM, μM (molar, millimolar, micromolar)
  - To represent: moles/L, 10^{-3} moles/L, 10^{-6} moles/L

- s


Periodic Table of the Elements
Atomic Number Symbol Name Atomic Mass
1 IA 11A
2 IIA 2A
3 IIIB 3B
4 IVB 4B
5 VB 5B
6 VIB 6B
7 VIIB 7B
8 9 VIII 8 10
11 IB 1B
12 IIB 2B
13 IIIA 3A
14 IVA 4A
15 VA 5A
16 VIA 6A
17 VIIA 7A
18 VIIIA 8A
1 H Hydrogen 1.008
2 He Helium 4.003
3 Li Lithium 6.941
4 Be Beryllium 9.012
5 B Boron 10.811
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998
10 Ne Neon 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.086
15 P Phosphorus 30.974
16 S Sulfur 32.066
17 Cl Chlorine 35.453
18 Ar Argon 39.948
19 K Potassium 39.098
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.88
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.933
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.39
31 Ga Gallium 69.732
32 Ge Germanium 72.61
33 As Arsenic 74.922
34 Se Selenium 78.09
35 Br Bromine 79.904
36 Kr Krypton 84.80
37 Rb Rubidium 84.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.94
43 Tc Technetium 98.907
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906
46 Pd Palladium 106.42
47 Ag Silver 107.868
48 Cd Cadmium 112.411
49 In Indium 114.818
50 Sn Tin 118.71
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe Xenon 131.29
55 Cs Cesium 132.905
56 Ba Barium 137.327
57-71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.948
74 W Tungsten 183.85
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.22
78 Pt Platinum 195.08
79 Au Gold 196.967
80 Hg Mercury 200.59
81 Tl Thallium 204.383
82 Pb Lead 207.2
83 Bi Bismuth 208.980
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn Radon 222.018
87 Fr Francium 223.020
88 Ra Radium 226.025
89-103
104 Rf Rutherfordium [261]
105 Db Dubnium [262]
106 Sg Seaborgium [266]
107 Bh Bohrium [264]
108 Hs Hassium [269]
109 Mt Meitnerium [268]
110 Ds Darmstadtium [269]
111 Rg Roentgenium [272]
112 Cn Copernicium [277]
113 Uut Ununtrium unknown
114 Fl Flerovium [289]
115 Uup Ununpentium unknown
116 Lv Livermorium [298]
117 Uus Ununseptium unknown
118 Uuo Ununoctium unknown
Lanthanide Series
57 La Lanthanum 138.906
58 Ce Cerium 140.115
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.24
61 Pm Promethium 144.913
62 Sm Samarium 150.36
63 Eu Europium 151.966
64 Gd Gadolinium 157.25
65 Tb Terbium 158.925
66 Dy Dysprosium 162.50
67 Ho Holmium 164.930
68 Er Erbium 167.26
69 Tm Thulium 168.934
70 Yb Ytterbium 173.04
71 Lu Lutetium 174.967
Actinide Series
89 Ac Actinium 227.028
90 Th Thorium 232.038
91 Pa Protactinium 231.036
92 U Uranium 238.029
93 Np Neptunium 237.048
94 Pu Plutonium 244.064
95 Am Americium 243.061
96 Cm Curium 247.070
97 Bk Berkelium 247.070
98 Cf Californium 251.080
99 Es Einsteinium [254]
100 Fm Fermium 257.095
101 Md Mendelevium 258.1
102 No Nobelium 259.101
103 Lr Lawrencium [262]

Normality

- Like molarity, but takes into account the stoichiometric ratios of reactants and products
  - e.g., charge, exchangeable H^+, exchangeable electrons
- Measured in equivalents per liter (eq/L or equ/L)
  - Or meq/L (=10^{-3} eq/L)

$$Normality = \frac{mass/L}{GEW}$$

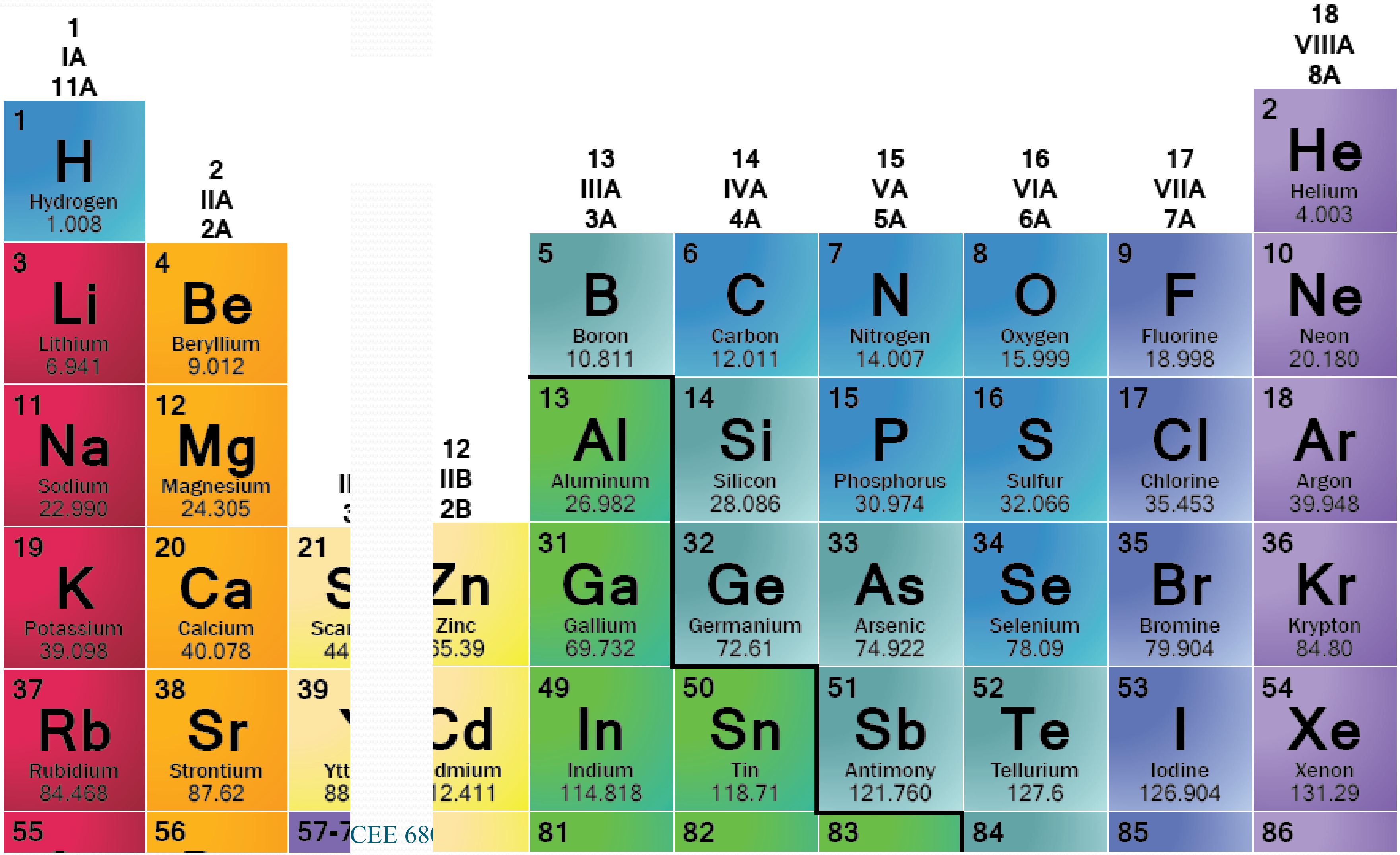
- And Z is an integer related to the number of exchangeable hydrogen ions, or electrons the chemical has, or its overall charge

$$GEW = GFW/Z$$

or

$$Normality = \frac{mass/L}{GFW}(Z)$$

Major metals and non-metals



"680 Periodic Table"

Element	Ocean residence time (log yr)	Predominant species	Seawater conc. (-log M)	River Water conc. (-log M)
H	4.5	H^+, H_2O	-1.74	-1.74
He			8.8	
Li	6.3	Li^+	4.6	
Be		$BeOH^+$	9.2	
B	7.0	H_3BO_4	3.39	
C	4.9	HCO_3^-	2.64	3.0
N	6.3	N_2, NO_3^-	1.97	
O	4.5	H_2O, O_2	-1.74	-1.74
F	5.7	F^-	4.17	5.3
Ne			8.15	
Na	7.7	Na^+	0.33	3.57
Mg	7	Mg^{+2}	1.27	3.77
Al	2	$Al(OH)_4^-$	7.1	
Si	3.8	H_4SiO_4	4.15	3.8
P	4	HPO_4^{-2}	5.3	
S	6.9	SO_4^{-2}	1.55	3.92
Cl	7.9	Cl^-	0.26	3.66
Ar			6.96	
K	6.7	K^+	1.99	4.23
Ca	5.9	Ca^{+2}	1.99	3.42
As		$HAsO_4^{-2}$	7.3	
Se	4	SeO_3^{-2}	8.6	
Br	8	Br^-	3.08	
Kr			8.6	
Sr	6.6	Sr^{+2}	4.05	
I	6	I^-, IO_3^-	6.3	
Ba	4.5	Ba^{+2}	6.8	

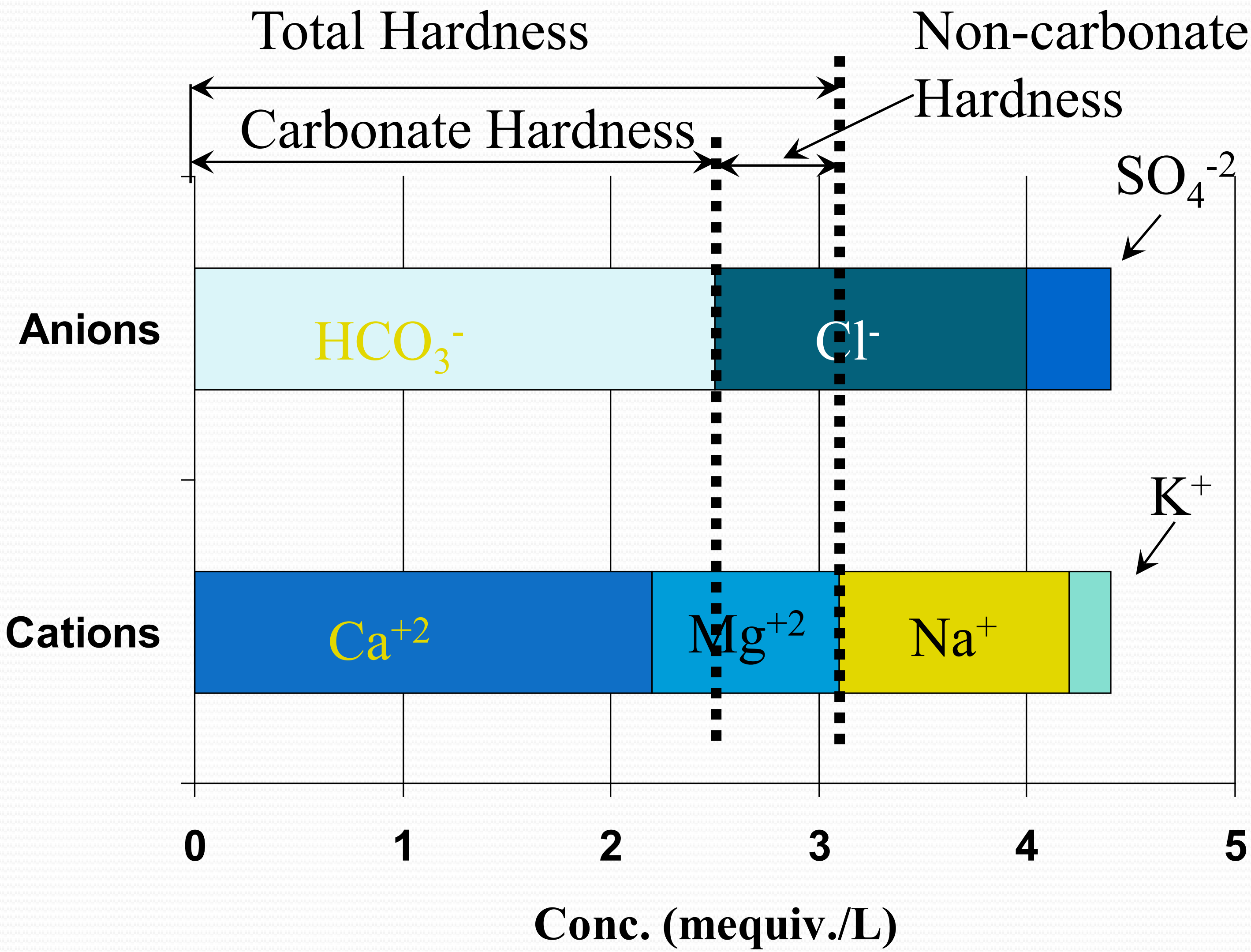
- Ocean residence time (log yr)
- Predominant species
- River Water conc. (-log M)
- Seawater conc. (-log M)

After S&M:Fig. 1.7, Pg. 10

"Complete" water analysis

Species	***mg/L***	***meq/L***
Bicarbonate	153	2.5
Chloride	53	1.5
Sulfate	19.2	0.4
Calcium	44	2.2
Magnesium	10.9	0.9
Sodium	25.3	1.1
Potassium	7.8	0.2

Anion-Cation Balance



Vaal River near Johannesburg

Parameter	Conc (mg/L)
Sodium	4.72
Potassium	0.91
Calcium	7.08
Magnesium	5.47
Chloride	4.54
Bicarbonate	50.44
Sulfate	7.39
TDS	78.69

Data from Mohr, 2015; site C1H001

- Calculate TDS based on measured ions
- Determine Cation - Anion balance
  1. Number of milli-equivalents/L of positive charge
  2. Number of milli-equivalents/L of negative charge
  3. Percent difference based on total milli-equivalents/L of ions

Vaal River near Johannesburg

Parameter	Conc (mg/L)
Sodium	4.72
Potassium	0.91
Calcium	7.08
Magnesium	5.47
Chloride	4.54
Bicarbonate	50.44
Sulfate	7.39
TDS	78.69

- Calculate TDS based on measured ions

Data from Mohr, 2015; site C1H001

$$calculated\ TDS = \sum Conc. = \mathbf{80.55}\frac{\boldsymbol{mg}}{\boldsymbol{L}}$$

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW
Sodium	4.72	23.0
Potassium	0.91	39.1
Calcium	7.08	40.1
Magnesium	5.47	24.3
Chloride	4.54	
Bicarbonate	50.44	
Sulfate	7.39	
TDS	78.69	

Data from Mohr, 2015; site C1H001

- Determine Cation - Anion balance
  1. First calculate molar concentration
  2. Number of milli-equivalents/L of positive charge

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM
Sodium	4.72	23.0	0.205
Potassium	0.91	39.1	0.023
Calcium	7.08	40.1	0.177
Magnesium	5.47	24.3	0.225
Chloride	4.54		
Bicarbonate	50.44		
Sulfate	7.39		
TDS	78.69		

Data from Mohr, 2015; site C1H001

- Determine Cation - Anion balance
  1. Molar (actually mM) concentration
  2. Number of milli-equivalents/L of positive charge

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge
Sodium	4.72	23.0	0.205	1
Potassium	0.91	39.1	0.023	1
Calcium	7.08	40.1	0.177	2
Magnesium	5.47	24.3	0.225	2
Chloride	4.54	35.5		
Bicarbonate	50.44	61.0		
Sulfate	7.39	96.1		
TDS	78.69			

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge	meq - Charge
Sodium	4.72	23.0	0.205	1	0.205
Potassium	0.91	39.1	0.023	1	0.023
Calcium	7.08	40.1	0.177	2	0.353
Magnesium	5.47	24.3	0.225	2	0.450
Chloride	4.54	35.5	0.128		
Bicarbonate	50.44	61.0	0.827		
Sulfate	7.39	96.1	0.077		
TDS	78.69				

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge	meq - Charge	total	
Sodium	4.72	23.0	0.205	1	0.205	1.032	
Potassium	0.91	39.1	0.023	1	0.023		cations
Calcium	7.08	40.1	0.177	2	0.353		
Magnesium	5.47	24.3	0.225	2	0.450		
Chloride	4.54						
Bicarbonate	50.44						anions
Sulfate	7.39						
TDS	78.69						

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW
Sodium	4.72	23.0
Potassium	0.91	39.1
Calcium	7.08	40.1
Magnesium	5.47	24.3
Chloride	4.54	35.5
Bicarbonate	50.44	61.0
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- Determine Cation - Anion balance
  1. First calculate molar concentration
  2. Number of milli-equivalents/L of positive charge
  3. Number of milli-equivalents/L of negative charge

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Parameter	Conc (mg/L)	GFW	mM
Sodium	4.72	23.0	0.205
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Calcium	7.08	40.1	0.177
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- Determine Cation - Anion balance
  1. Molar (actually mM) concentration
  2. Number of milli-equivalents/L of positive charge
  3. Number of milli-equivalents/L of negative charge

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge
Sodium	4.72	23.0	0.205	1
Potassium	0.91	39.1	0.023	1
Calcium	7.08	40.1	0.177	2
Magnesium	5.47	24.3	0.225	2
Chloride	4.54	35.5	0.128	-1
Bicarbonate	50.44	61.0	0.827	-1
Sulfate	7.39	96.1	0.077	-2
TDS	78.69			

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge	meq - Charge
Sodium	4.72	23.0	0.205	1	0.205
Potassium	0.91	39.1	0.023	1	0.023
Calcium	7.08	40.1	0.177	2	0.353
Magnesium	5.47	24.3	0.225	2	0.450
Chloride	4.54	35.5	0.128	-1	-0.128
Bicarbonate	50.44	61.0	0.827	-1	-0.827
Sulfate	7.39	96.1	0.077	-2	-0.154
TDS	78.69				

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge	meq - Charge	total	
Sodium	4.72	23.0	0.205	1	0.205		
Potassium	0.91	39.1	0.023	1	0.023	**1.032**	cations
Calcium	7.08	40.1	0.177	2	0.353		
Magnesium	5.47	24.3	0.225	2	0.450		
Chloride	4.54	35.5	0.128	-1	-0.128		
Bicarbonate	50.44	61.0	0.827	-1	-0.827	**-1.109**	anions
Sulfate	7.39	96.1	0.077	-2	-0.154		
TDS	78.69						

Data from Mohr, 2015; site C1H001

$$\% \, difference = 100 \frac{(1.032 - 1.109)}{(1.032 + 1.109)} = \mathbf{-3.6\%}$$

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW	mM	charge	meq - Charge	total	
Sodium	4.72	23.0	0.205	1	0.205		
Potassium	0.91	39.1	0.023	1	0.023	**1.032**	cations
Calcium	7.08	40.1	0.177	2	0.353		
Magnesium	5.47	24.3	0.225	2	0.450		
Chloride	4.54	35.5	0.128	-1	-0.128		
Bicarbonate	50.44	61.0	0.827	-1	-0.827	**-1.109**	anions
Sulfate	7.39	96.1	0.077	-2	-0.154		
TDS	78.69						

Data from Mohr, 2015; site C1H001

$$calculated\ TDS = \sum Conc. = \mathbf{80.55\frac{mg}{L}}$$

Common Constituents

- N, P, and S containing compounds are often expressed in terms of their elemental concentration
- Examples
  - 66 mg of $(NH_4)_2SO_4$ added to 1 L of water
  - 85 mg of $NaNO_3$ added to 1 L of water

Example: element/group conc.

- Consider a solution of Ammonium Sulfate prepared by dissolving 66 g of the anhydrous compound in water and diluting to 1 liter. What is the concentration of this solution in:
  - a) g/L?
  - b) moles/L?
  - c) equivalents/L?
  - d) g/L as sulfate?
  - e) g/L as N?

Example (cont.)

- a) 66 g/L
- b) The gram formula weight of ammonium sulfate is 132 g/mole. So, using equation 2.7, on gets:
  - Molarity = (66 g/L)/(132 g/mole) = 0.5 moles/L or 0.5 M.
- c) Without any specific information regarding the use of this solution, one might simply presume that either the sulfate group or the ammonium group will be the reacting species. In either case, Z should be equal to two (product of the oxidation state times the number of groups). So:
- Normality = 0.5 moles/L * 2 equivalents/mole
- = 1 equivalent/L or 1.0 N or N/1.

Example (cont.)

- d) The GFW for sulfate is:
  - GFW = 32 + 4*16 = 96.
- The molarity of sulfate is:
  - Molarity = 0.5 moles-$(NH_4)_2SO_4$/L * 1 mole-SO_4/mole-$(NH_4)_2SO_4$
  - = 0.5 moles-SO_4/L
- Then, one :gets
  - mass/L = Molarity * GFW
    = 0.5 moles-SO_4/L * 96 g-SO_4/mole-SO_4
  - = 48 g-SO_4/L

Example (cont.)

- e) The GFW for nitrogen is simply 14:
  - The molarity of nitrogen is:
    - Molarity = 0.5 moles-$(NH_4)_2SO_4$/L * 2 moles-N/mole-$(NH_4)_2SO_4$
    - = 1 mole-N/L
  - Again, one gets:
    - mass/L = Molarity * GFW = 1 mole-N/L * 14 g-N/mole-N
    - = 14 g-N/L or 14 g NH_3-N/L

Calcium carbonate units

- Used for major ion concentrations in drinking waters
  - Alkalinity
  - Hardness
- Since $CaCO_3$ is divalent (Z=2) and its GFW is 100 g, its GEW is 50 g
  - 50 g/equivalent or 50 mg/meq
  - 50,000 mg/equivalent

Some important isotopic abundances

- CH&O

Element	Isotope	Percentage natural abundance
Carbon	^{12}C	98.892
	^{13}C	1.108
	^{14}C	Trace
Hydrogen	^{1}H	99.985
	^{2}H	0.015
	^{3}H	Less than 10^{-16}
Oxygen	^{16}O	99.763
	^{17}O	0.037
	^{18}O	**0.2**

Source: [6]

Atomic Mass I

- One Dalton is defined as the mass of one-twelfth of a Carbon 12 atom
  - Therefore a ^{12}C weighs exactly 12 Da

$$1Da = \tfrac{1}{12} M_{^{12}C} = {}^{1}\!/_{N_A}$$

$$= 1.66053878x10^{-27}\,kg$$

- *Sub atomic particles*
  - m_{proton} = 1.007825 Da
  - $m_{neutron}$= 1.008665 Da

Atomic Mass II

- Mass Defect (m_{def}) and binding energy (ΔE) for a single atom is given by:

$$m_{def} = m_s - m_b = Zm_p + Nm_n - m_b$$

$$\Delta E = m_{def} c^2$$

- where
  - c is the speed of light,
  - m_s is the mass of the separated nucleons
  - m_b is the mass of the bound nucleus
  - Z is the atomic number of the bound nucleus
  - m_p is the mass of one proton
  - N is the number of neutron
  - m_n is the mass of one neutron.

Atomic Mass III

- **example: a deuteron**
  - A deuteron is the nucleus of a deuterium atom, and consists of one proton and one neutron. The experimentally-measured masses of the constituents as free particles are
    - m_{proton} = 1.007825 Da; m_{neutron}= 1.008665 Da;
    - $m_{\text{proton}} + m_{\text{neutron}}$ = 1.007825 + 1.008665 = 2.01649 Da.
    - The mass of the deuteron (^{2}H, also an experimentally measured quantity) = 2.014102 Da.
  - The mass difference = 2.01649−2.014102 = 0.002388 Da.
    - Since the conversion between rest mass and energy is 931.494MeV/Da, a deuteron's binding energy is calculated to be 0.002388 Da × 931.494 MeV/Da = 2.224 MeV.

Isotopes

Chart of the Nuclides

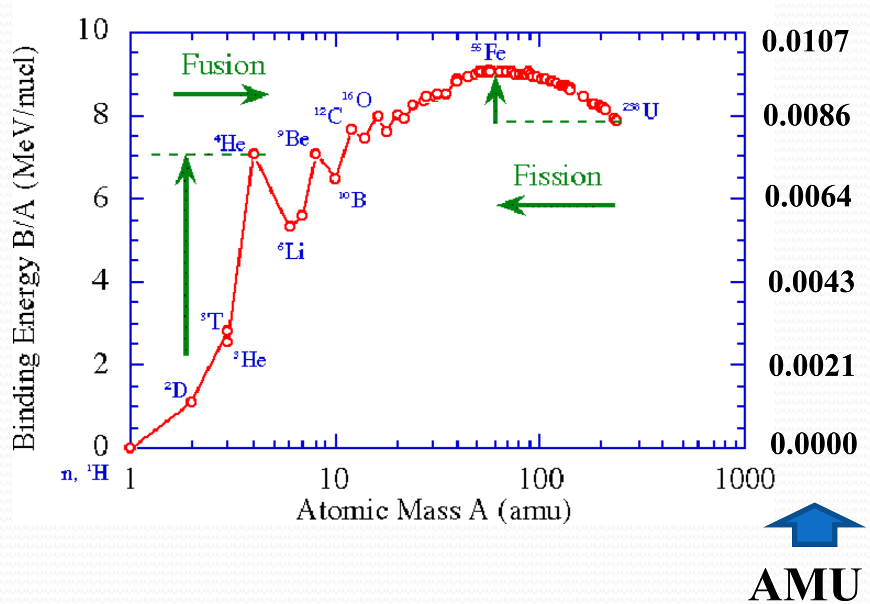
(Including the first 8 elements up to Oxygen)

protons \ neutrons	0	1	2	3	4	5	6	7	8	9	10	11	12
8						O 13 .0087s	O 14 71s	O 15 124s	O 16 99.759	O 17 0.037	O 18 0.204	O 19 29s	O 20 14s
7						N 12 0.011s	N 13 9.96m	N 14 99.63	N 15 0.37	N 16 7.1s	N 17 4.14s	N 18 0.63s	
6				C 9 0.13s	C 10 19s	C 11 20.5m	C 12 98.89	C 13 1.11	C 14 5730y	C 15 2.25s	C 16 0.74s		
5				B 8 0.78s	B 9 $3x10^{-19}$s	B 10 19.78	B 11 80.22	B 12 0.020s	B 13 0.019s				
4			Be 6 $4x10^{-21}$s	Be 7 53d	Be 8 $3x10^{-16}$s	Be 9 100	Be10 $2.7x10^{6}$y	Be11 13.6s	Be12 0.011s				
3			Li 5 10^{-21}s	Li 6 7.42	Li 7 92.58	Li 8 0.85s	Li 9 0.17s						
2		He 3 .00013	He 4 100	He 5 $2x10^{-21}$s	He 6 0.81s		He 8 0.122s						
1	H 1 99.985	H 2 0.015	H 3 12.26y										

Mass Defects and Elemental mass

- Mass of Carbon

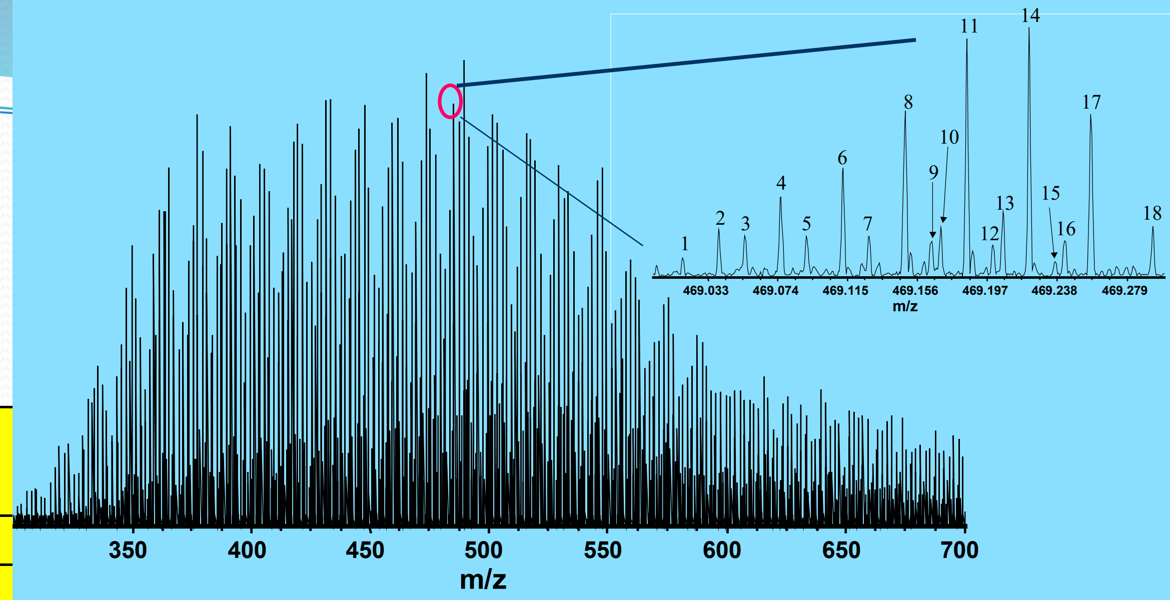
Particle	Mass (kg)	Mass (amu)
neutron	1.674929×10^{-27}	1.008664
proton	1.672623×10^{-27}	1.007276
electron	9.109390×10^{-31}	0.00054858



^{12}C-Mass defect = 6 * 1.008664 amu + 6 * 1.007276 amu + 6 * 0.00054858 amu - 12.000 amu = 0.098931 amu

Isotope	protons	neutrons	electrons	sum	measured	mass defect	per nucleon	Abundance	product
C-12	6	6	6	12.098931	12	0.098931	0.0082443	98.9%	11.8716
C-13	6	7	6	13.107595	13.003355	0.104240	0.0080185	1.1%	0.1391
									12.0107

Exact Mass



Peak #	Proposed molecular formula	Observed values	Theoretical values	
1	$C_{25}H_{10}O_{10}$	469.02018	469.02012	
2	$C_{22}H_{14}O_{12}$	469.04118	469.04125	
3	$C_{26}H_{14}O_9$	469.05646	469.05651	0.1
4	$C_{23}H_{18}O_{11}$	469.07763	469.07764	0
5	$C_{27}H_{18}O_8$	469.09288	469.09289	0
6	$C_{24}H_{22}O_{10}$	469.11401	469.11402	0
7	$C_{28}H_{22}O_7$	469.1293	469.12928	0
8	$C_{25}H_{26}O_9$	469.15042	469.15041	0
9	$C_{29}H_{26}O_6$	469.16576	469.16566	-0.2
10	$C_{22}H_{30}O_{11}$	469.17151	469.17154	0.1
11	$C_{26}H_{30}O_8$	469.18681	469.18679	0
12	$C_{30}H_{30}O_5$	469.20201	469.20205	0.1
13	$C_{23}H_{34}O_{10}$	469.20789	469.20792	0.1
14	$C_{27}H_{34}O_7$	469.22316	469.22318	0
15	$C_{31}H_{34}O_4$	469.23838	469.23843	0.1
16	$C_{24}H_{38}O_9$	469.24423	469.24431	0.2
17	$C_{28}H_{38}O_6$	469.25949	469.25956	0.2
18	$C_{29}H_{42}O_5$	469.29584	469.29595	0.2

- High resolution mass spectrometer
- Aquatic natural organic matter
  - Nominal mass of 469 for negative ion (M-H)
- 18 isotopically pure possibilities for "M"
  - Many with same #s of protons & neutrons
  - Different mass defects due to different nuclear binding energies

- To next lecture