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 6.02×10^{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

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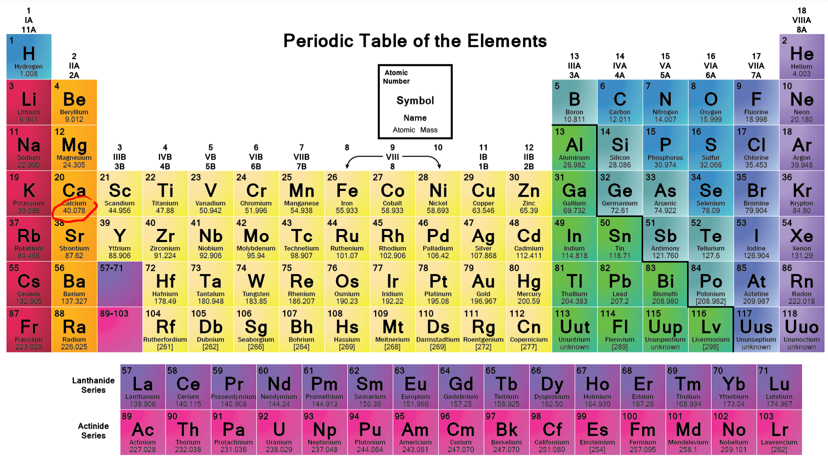


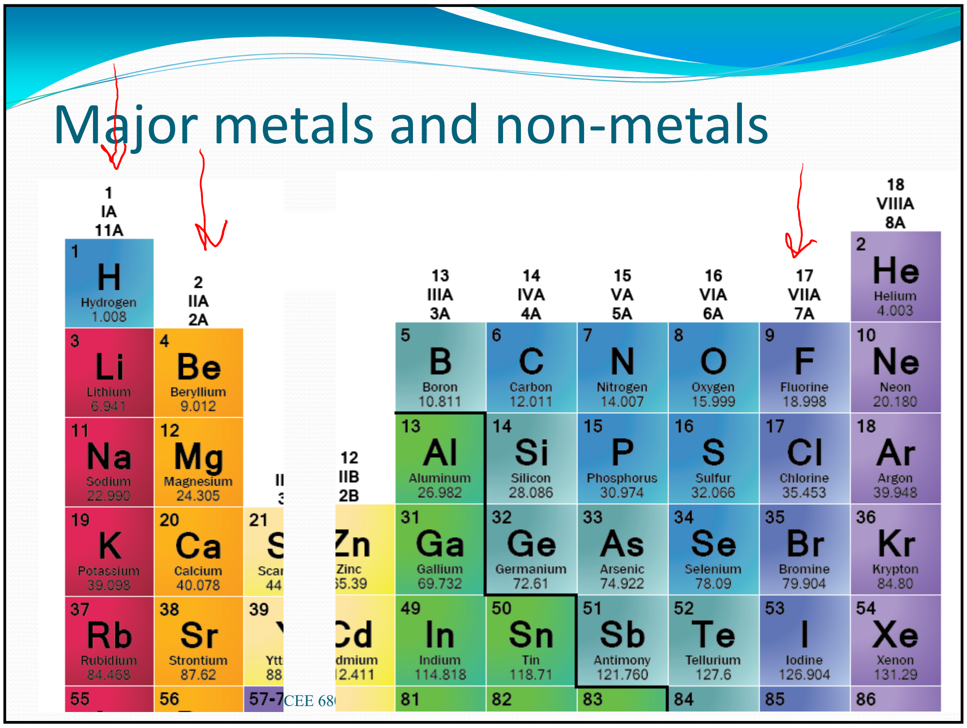
Normality

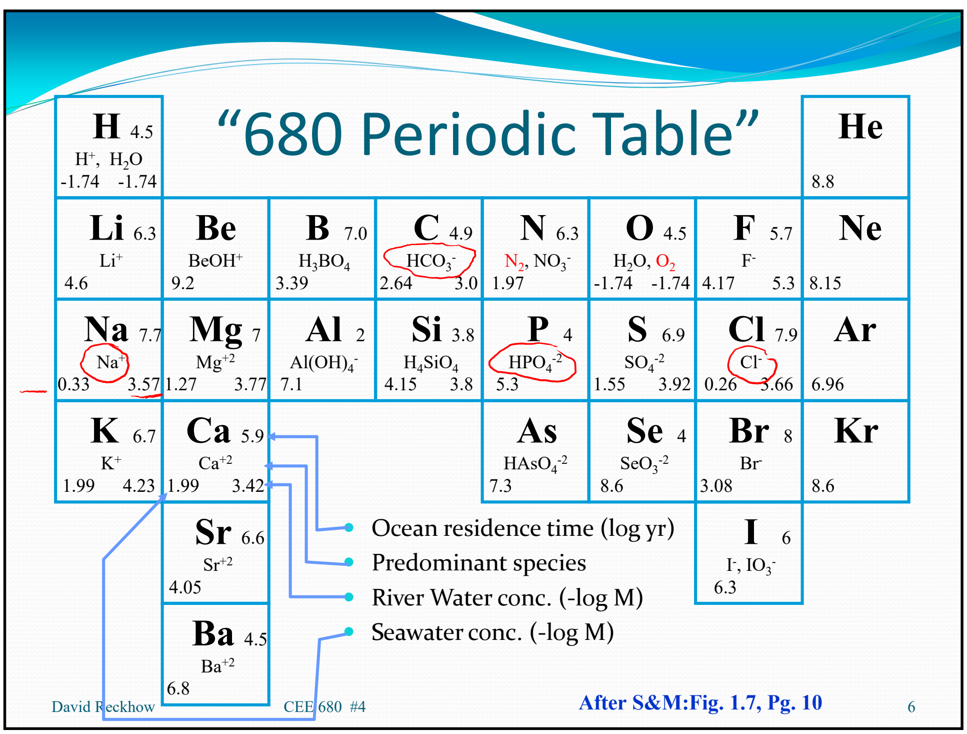
- Like molarity, but takes into account the stoichiometric ratios of reactants and products
  - e.g., charge, exchangeable H^+, exchangeable electrons
- Measured in equivalents per liter (eq/L or equ/L)
  - Or meq/L (=10^{-3} eq/L)

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

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

$$GEW = GFW/Z \quad \text{or} \quad Normality = \frac{mass/L}{GFW}(Z)$$


Major metals and non-metals
1 IA 11A
2 IIA 2A
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
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
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
56
57-7
81
82
83
84
85
86


"680 Periodic Table"
H 4.5 H+, H2O -1.74 -1.74
He 8.8
Li 6.3 Li+ 4.6
Be BeOH+ 9.2
B 7.0 H3BO4 3.39
C 4.9 HCO3- 2.64 3.0
N 6.3 N2, NO3- 1.97
O 4.5 H2O, O2 -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 H4SiO4 4.15 3.8
P 4 HPO4-2 5.3
S 6.9 SO4-2 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 HAsO4-2 7.3
Se 4 SeO3-2 8.6
Br 8 Br- 3.08
Kr 8.6
Sr 6.6 Sr+2 4.05
Ba 4.5 Ba+2 6.8
I 6 I-, IO3- 6.3
Ocean residence time (log yr)
Predominant species
River Water conc. (-log M)
Seawater conc. (-log M)
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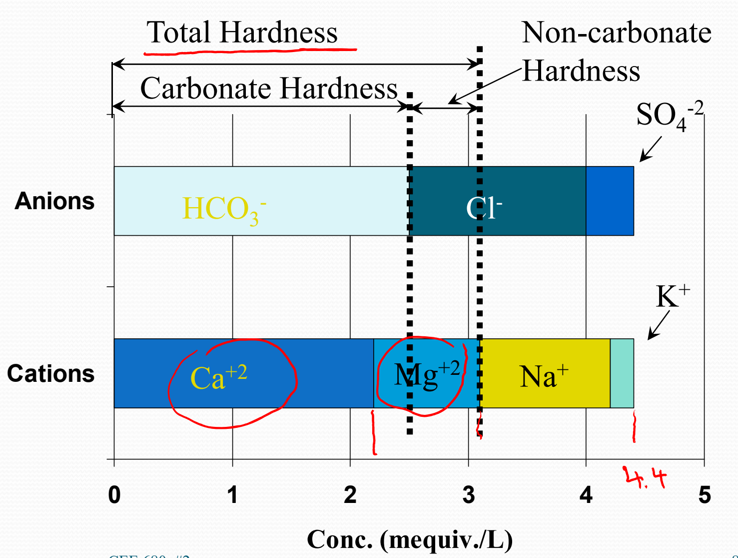
After S&M:Fig. 1.7, Pg. 10
6

"Complete" water analysis

SO_4^{-2}
32+4(16)
96
GFW

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

- 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

Data from Mohr, 2015; site C1H001

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

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

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	

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

1.03 ?

Data from Mohr, 2015; site C1H001

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		

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

Data from Mohr, 2015; site C1H001

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	
Potassium	0.91	39.1	0.023	1	0.023	**1.032**
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					
Sulfate	7.39					
TDS	78.69					

cations

anions

Data from Mohr, 2015; site C1H001

Vaal River near Johannesburg

Parameter	Conc (mg/L)	GFW
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Sulfate	7.39	96.1
TDS	78.69	

- 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

HCO_3^-

SO_4^{-2}

1.109

Data from Mohr, 2015; site C1H001

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
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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

Data from Mohr, 2015; site C1H001

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

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

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?

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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.

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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

Amu

$$1Da = \tfrac{1}{12} M_{^{12}C} = \frac{1}{N_A}$$

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

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

$E = mc^2$

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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.

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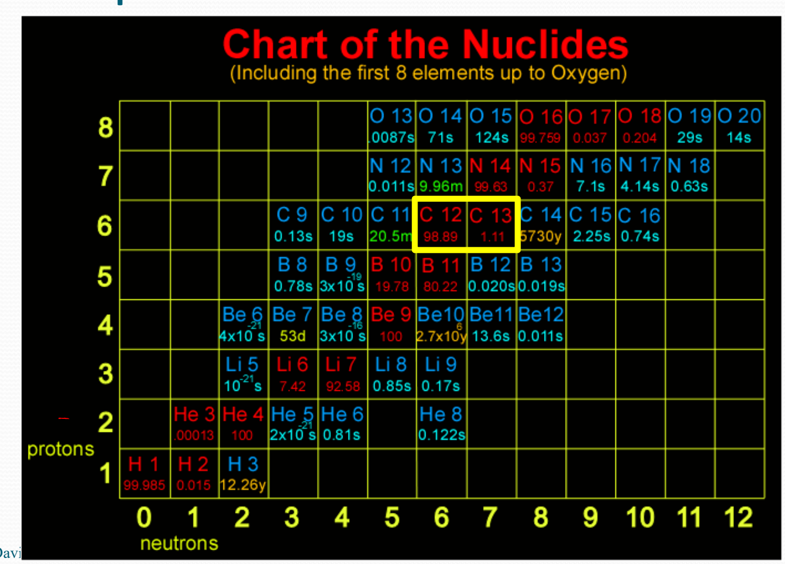
Atomic Mass III

- **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_{proton} + $m_{neutron}$ = 1.007825 + 1.008665 = 2.01649 Da.
    - The mass of the deuteron (^2H, 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.

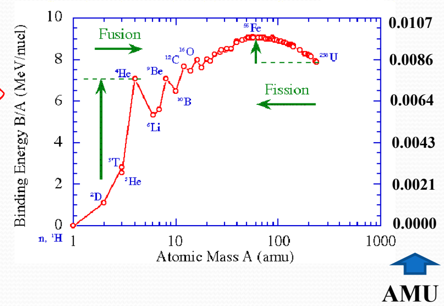
Isotopes



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

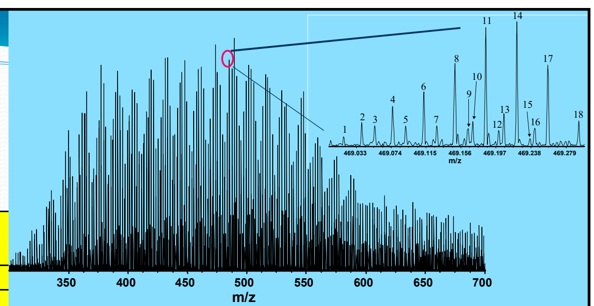


^{12}C-Mass defect = 6 * 1.008664 amu + 6 * 1.007276 amu + 6 * 0.00054858 amu - 12.000 amu = 0.098931 amu

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