Chapter 2

Atoms and the Atomic Theory

Origin of the idea of atoms

Starts with the ponderings about Nature and existence in pre-Socratic Greek philosophy (600 BC – 425 BC)

Their work was called "Natural Philosophy"

In fact, until the 19th century the term "Natural Philosophy" was the term used for "Science", or the practice of studying Nature.

What you normally hear/read about how ancient Greek philosophers arrived at the idea of atoms is <u>almost certainly wrong</u>.

2

Pre-Socratic Greek philosophers arrived at the concept of atoms because there was no other way to explain the existence of change! Parmenides: Change is not real; it's an illusion! $A \rightarrow B$ means that A is disappearing into nothing, and B is appearing out of nothing $A \rightarrow nothing$ $nothing \rightarrow B$ "Something" cannot turn into "Nothing", and

"Nothing" cannot turn into "Something" Therefore, change cannot be real!

- Solid reasoning. Pretty bold. But kind of unacceptable.
- But these well-reasoned conclusions had to be proven wrong. That led to the idea of atoms.

3

Atomists:

1

Democritus and the "atomists":

- Parmenides is correct in stating that parts of the universe can't just disappear, or appear out of nothing.
- But we <u>can</u> have changes and transformations, if things are made up of tiny, invisible particles that rearrange and recombine.
- Those fundamental, permanent, indivisible particles (atoms) themselves don't change (just like Parmenides concluded), <u>but</u> their rearrangements and re-combinations are the cause for observed change.
- Different atoms can come together to form a new substance.
- Each substance has its characteristic particle, and the attributes of these particles determine the attributes of the substance they make up.

4

Oh, by the way, there has to be a void (empty space) for atoms to move around and do their rearranging.



Paraphrasing Democritus: "Reality is nothing but the atoms moving around in the void"

The first mechanical view of universe

-- originally expressed much more poetically (literally in poem form)

So, the ancient (460-400 BC) Greek concept of atom was not simply an intuitive guess or idle speculation

It was the inescapable result of impressively disciplined thinking by a few generations of philosophers.

<u>They had to</u> invent the idea of atoms to explain the existence of change

Usually identified with the modern idea of atom

But it's deeper than that: it's about particles of "stuff"

Very famous physicist Richard Feynman (1918-1988)

From Feynman Lectures:

"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, <u>what statement would contain the most</u> <u>information in the fewest words?</u>

I believe it is the *atomic hypothesis* (or the atomic *fact*, or whatever you wish to call it) that *all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*. In that one sentence, you will see, there is an *enormous* amount of information about the world, <u>if just a little</u> <u>imagination and thinking are applied</u>. "

http://www.feynmanlectures.caltech.edu/I_01.html

7

Now, back to chemistry and on to the (early) modern era ...

9

Robert Boyle was the first "chemist" (1661)

- Used the "scientific method"
- Performed quantitative experiments on the pressure and volume of gases

Universe is made up of ~5% ordinary matter, ~27% Dark Matter and

Whether through intuition, or by thinking along the lines of ancient

Dark Matter density varies across the universe, and ... Physicists are looking for Dark Matter "particles",

even though they know nothing about Dark Matter

They aren't looking for particles of Dark Energy (the

mysterious "thing" that makes the universe expand

We don't know what the latter two really are, but ...

"Dark Energy" appears to be a constant, and ...

~68% Dark Energy

Greek philosophers:

faster and faster)

 Developed the first experimental definition of an element:

A substance is an element unless it can be broken down into two or more simpler substances

10

8

Three Important Laws:

Law of conservation of mass (Lavoisier):

Mass is neither created nor destroyed in a chemical reaction.

Law of definite proportion (Proust):

A given compound always contains exactly the same proportion of elements by mass.

Law of multiple proportions (Dalton):

When two elements form a series of compounds, the ratios of the masses of the second element that combine with a fixed amount of the first element will be ratios of small whole numbers.

Law of conservation of mass (Lavoisier):

Mass is neither created nor destroyed in a chemical reaction.

A plant grows from a tiny seed up to a huge tree. Does this violate the Law of Conservation of Mass? Explain. Law of definite proportion (Proust):

A given compound always contains exactly the same proportion of elements by mass.

Question:

According to the Law of Definite Proportions:

- a) If the same two elements form two different compounds, they do so in the same ratio
- b) It is not possible for the same two elements to form more than one compound
- c) The ratio of the masses of the elements in a compound is always the same
- d) The total mass after a chemical change is the same as before the change.

14

A sample of chemical X is found to contain 5.0 grams of oxygen, 10.0 grams of carbon, and 20.0 grams of nitrogen. The law of definite proportion would predict that a 70 gram sample of chemical X should contain how many grams of carbon?

a) 5.0 grams
b) 7.0 grams
c) 10. grams
d) 15 grams
e) 20 grams

15

13

Law of multiple proportions (Dalton):

When two elements form a series of compounds:

For a <u>fixed amount of one element</u>, <u>the amounts of the **other**</u> element in those compounds will be in **ratios of "small" whole numbers**.

1:2, 1:3, 2:3, 5:2 etc.

16

Law of multiple proportions (Dalton):

When two elements form a series of compounds:

For a fixed amount of one element,

the amounts of the **other** element in those compounds will be in **ratios of "small"* whole numbers**.

1:2, 1:3, 2:3, 5:2 etc.

Compounds known at that time had at most a few atoms of any element in their formulas. Quantitative methods were not good enough to deal with larger numbers anyway. But the principle is still valid, even when the numbers are large, and our methods are accurate and precise enough to tell apart 133:100 from 4:3

Example

- Carbon and oxygen make two compounds. Their molecules are composed of:
- 1 carbon with 1 oxygen for "Carbon monoxide"
- 1 carbon with 2 oxygens for "Carbon dioxide"

Without knowing anything about the mass of carbon and oxygen atoms, we can say that "carbon dioxide" has twice as much oxygen for a given amount of carbon as "carbon monoxide".

How about the amount of carbon per oxygen?

Example (cont.)

1 carbon with 1 oxygenfor "Carbon monoxide"1 carbon with 2 oxygensfor "Carbon dioxide"Now we are comparing the amount of carbon per oxygen in
the two compounds. It's a bit trickier.

We can make it easier to think about by making the number of oxygens the same. So we take two carbon monoxide molecules, corresponding to 2 oxygens.

2 carbons per 2 oxygens for "Carbon monoxide" 1 carbon with 2 oxygens for "Carbon dioxide"

Carbon dioxide has half as much carbon for a given amount of oxygen as carbon monoxide

19

s it ok to also say "In A, there is half as much O per each atom of Cr"?
Yes. For a given amount of Cr, A has half as much O as CrO_2 .
The sample size doesn't matter.
The amount of Cr we are considering doesn't change the relative amounts of oxygen in the two compounds.
f one compound is half as rich in oxygen as the other compound, that fact won't change with sample size.
For any given amount of Cr, compound A has half as much O as CrO ₂ .
After all, we could consider the amount of O for a mass of Cr equal to the mass of 1 Cr atom. It's still "for a given amount of Cr".
So the relative amounts applies equally to the number of atoms contained in the two compounds.
1 O atom instead of 2 O atoms per Cr atom So the formula for A can be: CrO

21

A compound of chromium (symbol: Cr) and oxygen (symbol: O) has the formula CrO₂. Using the Law of Multiple Proportions, guess the formulas for the other compounds of Cr and O, using the data provided in the table below. Mass of Cr (g) Mass of O (g) Compound CrO_2 52 32 Compound A 39 12 Compound B 26 24 0.615 g O 32 g O In CrO₂, there is 32 g of O per 52 g of Cr 52 g Cr 1 g Cr 12 g O 0.308 g O In A, there is 12 g of O per 39 g of Cr 39 g Cr 1 g Cr In A, there is 0.308 g of O per gram of Cr 0.308 g ≈ 1/2 Compared to 0.615 g O per gram of Cr in CrO₂ 0.615 g In A, there is half as much O per gram of Cr as in CrO₂ So.

20

Now guess the formula for Compound B using the same table and the same reasoning

Compound	Mass of Cr (grams)	Mass of O (grams)					
CrO ₂	52	32					
Compound A	39	12					
Compound B	26	24					

22

24

Which of the following pairs of compounds can be used to illustrate the law of multiple proportions?
A) NH₄ and NH₄Cl
B) ZnO₂ and ZnCl₂
C) H₂O and HCl
D) NO and NO₂

Law of Definite Proportions did give a hint that matter was acting "as if" it were made of discrete particles (atoms)
-- at least to those who liked the idea of atoms.
-- Otherwise why else would two elements come together in a definite ratio of masses?
-- Think Lego pieces that have different masses

- On the other hand, it was reasonable to think that there might be some other explanation.
- After all, the mass ratios were nothing special. The numbers didn't look like "counts" (or rather, ratios of counts of particles.)

- Law of Multiple Proportions all of a sudden produced these simple ratios of small integers relating different compounds of the same two elements.
- That was a much stronger hint that different elements were combining using discrete particles (atoms)
- One had to be irrationally opposed to the idea of atoms to ignore the hint.
- In fact it was stated by Dalton as one of the predictions by his atomic theory.

Dalton's Atomic Theory (1808)

- Each element is made up of tiny particles called atoms.
- The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways. Not quite, we now know there are "isotopes"
- Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.
- Chemical reactions involve reorganization of the atoms—changes in the way they are bound together.
- The atoms themselves are not changed in a chemical reaction.

26





Avogadro's theory was our first true connection to the atomic world

Chemists did not suspect that gases like hydrogen, oxygen, chlorine, etc. were made of diatomic molecules

- If you don't know how heavy each oxygen atom and each hydrogen atom is,
- And you see that 1 g of hydrogen combines with 8 grams of oxygen to form water,
- Assuming the simplest formula for water (HO), you conclude that oxygen atoms are 8 times as heavy as hydrogen atoms





So,

Avogadro's "hypothesis", for the first time, made a connection between macroscopic (human scale) measurements and the number of particles in a sample. Until early 20th century (1900s), atoms were still a "working assumption", as far as physicists were concerned.

- Chemists were sure atoms actually existed
- Physicists insisted on more direct evidence
 All they could say was that "matter behaves as if it is made of atoms"

Either way, nobody knew what they were made of, or their internal structure, if any.

34





- Those negative particles had to be coming from atoms, if all matter were made of atoms
- Being negatively charged, they could not be the entire atom
 - Atoms must be electrically neutral because materials are normally neutral.
- If the atom had negatively charged particles, it must have had a **positively charged part too**.





Robert Millikan (1909)

- · Performed experiments involving charged oil drops.
 - Made microscopic oil droplets; determined their size
 - Calculated their weight from their size and density
 - Charged microscopic oil droplets with random charges
 - The electrical force needed to balance the droplets against gravity let him calculate the charges on droplets
 - Charges turned out to be multiples of a certain small number
 - That had to be the smallest possible charge: i.e. the charge of an electron
- Charge on a single electron = 1.6×10^{-19} Coulombs
- Calculated the mass of the electron (9.11 \times 10⁻³¹ kg) from the charge-to-mass ratio measured by Thomson.

Don't memorize numbers like that just because they are on the slides

39

Henri Becquerel (1896)

 Discovered radioactivity by observing the spontaneous emission of radiation by uranium.

But before we come to Rutherford ...

- Using a magnetic field he found that there were three kinds of radiation:
 - negatively charged
 - positively charged
 - neutral

40

38

Ernest Rutherford (1911)

Classified three types of radioactive emission based on their penetrating power (instead of charge, as Becquerel did)

- Alpha (α)
 - -- a particle with a +2 charge (least penetrating)
 - -- much heavier than other types of radiation
- Beta (β) a high speed electron (-1 charge)
- Gamma (Y) high energy light (neutral) (most penetrating)

There are other kinds of radiation too

Ernest Rutherford (1911)

- Showed "plum pudding" model to be wrong
- · Found that:
 - The atom has a very dense center with (+) charge: nucleus
 - Electrons travel around the nucleus, at large distances compared with the size of the nucleus
- And here is how he did that:





44

Neutrons

- hypothesized by Rutherford in 1920
- discovered experimentally in 1932 by James Chadwick
- have no electric charge (neutral)
- · mass and size similar to proton; very slightly heavier
- Act as glue holding the positively charged protons together
- There is a special nuclear force, the <u>"strong nuclear force"</u> <u>between neutrons and protons</u> that can overcome the electrostatic repulsion between positively charged protons.
- Without neutrons the repulsion between the (+) charged protons would break the nucleus apart

45

SU, the att	
Electrons:	 outside the nucleus
	negatively charged
	 much lighter than protons and neutrons
	 spread over a much larger volume than the nucleus
Protons:	in the nucleus
	 positive charge equal in magnitude to the electron's negative charge.
	 tiny but heavy (dense)
Neutrons:	in the nucleusno charge

46



- **Small** compared with the overall size of the atom.
- Extremely dense; accounts for almost all of the atom's mass

Each proton or neutron is ~1850 times heavier than an electron

- -- we normally ignore the mass of electrons
- -- proton and neutron masses are slightly different
- -- and their mass changes slightly depending on nucleus they are in







50

Isotopes

- Atoms with the <u>same number of protons</u>
 same element
 - but different numbers of neutrons.
- Isotopes show virtually identical chemical properties because <u>chemistry is done by the electrons</u>. (the isotopes of the lightest elements like H or Li have measurable chemical differences, but the reasons for that is beyond the scope of the course)
- In nature most elements are mixtures of isotopes. The relative abundances of isotopes on Earth are fairly well fixed

51









Atomic masses ("atomic weight")

"Atomic mass" of an element is an average quantity

- It is a weighted average of isotopic masses
- · because elements almost always have more than one isotope with significant abundance

But before we deal with averaging isotopic masses, let's understand the "atomic mass unit" (used to be denoted by *a.m.u*, nowadays just *u*)

55

Atomic Mass Unit

Atomic mass unit is meant to approximate the atomic mass number.

But in general it can't be exactly equal to it.

Things would be simple if:

- protons and neutrons had the same exact mass
- and their masses did not depend on the kind of nucleus they are in
- Then, knowing the proton and neutron mass, we could calculate the mass of any isotope
 - ¹³C would have a mass of exactly 13*u*
 - ³⁵Cl would have a mass of exactly 35*u*

56

Alas.

- protons and neutrons have slightly different masses,
- and their exact masses depend on the kind of nucleus they are in

nuclear energies involved in binding these particles are large enough to show up as measurable mass, because E=mc²



Atomic Mass Unit

Atomic Mass Unit

57

Atomic Mass Unit So, the mass of an atom, measured in atomic mass units (u),

- instead of simply corresponding to the number of protons and neutrons in a nucleus (i.e. "mass number"),
- needs to be "calibrated" on a particular nucleus
 - ▶ ¹²C was chosen
- It is almost equal to the mass number, but not quite, for all elements and isotopes, except the calibration isotope ¹²C, whose mass is <u>defined</u> to be 12u

58

• So,

- ¹²C is the standard for atomic mass, with a mass of exactly 12 atomic mass units (u).
- · The masses of all other atoms are measured relative to this standard.
- So, if ⁴⁸Ti is measured to be 3.9957 times heavier than ¹²C,
- > then its atomic mass is 3.9957x12 = 47.948u

Atomic Mass

Elements occur in nature as mixtures of isotopes

Atomic Mass Unit

Atomic mass of an element

(as opposed to an isotope)

is a weighted average of isotopic masses

Atomic Mas



Even though natural carbon does not contain even a single atom with mass 12.01, for stoichiometric purposes, we can consider carbon to be composed of only one type of atom with a mass of 12.01 (like our average jellybean) This enables us to count atoms of natural carbon by weighing a sample of carbon.

62

Atomic Mass	Atomic Mas
Practice	Practice
An element consists of 62.60% of an isotope with mass 186.956 u and 37.40% of an isotope with mass 184.953 u. Calculate the average atomic mass and identify the element.	Indium has atomic number 49 and atomic mass 114.8 u. Naturally occurring indium contains a mixture of indium-112 and indium-115, respectively. What is the approximate ratio of the indium-112 abundance to that of the indium-115?
Average Atomic Mass = (0.6260)(186.956 u) + (0.3740)(184.953 u) = 186.2 u	Remember: Isotopic mass numbers can be used to approximate isotopic masses.
Phonium (Po)	a) 7:93
Kileiliulii (Ke)	b) 25:75
We can identify an element by its average atomic mass (the "atomic mass" reported in the periodic table)	c) 50:50
(the atomic mass reported in the periodic table)	d) 75:25
It's not the same as identifying the element from the isotopic mass (which we can't)	e) 93:7
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63



The concept of "mole"

In chemistry it's the count of atoms that matter.

2 hydrogen atoms combined with 1 oxygen atom form a water molecule.

We can directly measure masses, but chemistry doesn't care about masses. It cares about individual atoms and their counts.

We need a concept that keeps track of the number of atoms (or the entities they form, like molecules):

1 mole = 6.02214076 × 10²³ entities

Avogadro's Number (defined to be exact in 2019)

Avogadro's number is now defined exactly as $6.02214076 \times 10^{23}$, but is usually used with 3 or 4 significant figures:

6.022 × 10²³ entities/mole

- "elementary entities", or "characteristic units"
- Not just atoms or molecules
- Can be atoms, ions, molecules, formula units, electrons, protons, neutrons, photons, etc.

67

The concept of "mole" and molar mass

The unit "mole" represents a count. Just like "dozen" represents a count.

So, in principle, we can use "mole" to count things other than atoms or molecules:

1 mole of marbles, that is 6.022 $\,\times\,$ 10^{23} of them, can cover the surface of the Earth to a depth of 50 miles

If you had 1 mole of dollars, you could spend 1 billion dollars every second and you wouldn't run out of money for 19 million years

68

The concept of "mole" and molar mass

The concept of "mole"

But why 6.022 x 10²³ particles per mole?

Why not a simpler, smaller number?

We need it to be of the order of 10^{23} because atoms are extremely light, and it takes that many of them to have the kind of masses we normally deal with (i.e. human-scale quantities)

Why 6.022..., and not 1?

It allows us to calculate the mass of 1 mole (molar mass) directly from atomic masses. We use the same numbers but use grams instead of a.m.u!

69

The concept of "mole" and molar mass

1 carbon-12 atom has a mass of **12 a.m.u.**

 $6.022 \ x \ 10^{23} \ carbon-12 \ atoms$ (i.e. 1 mole of $^{12}\text{C})$ have a mass of $12 \ grams$

The atomic mass of iron (Fe) is **55.845 a.m.u** (the average mass of iron atoms is 55.845 a.m.u.)

6.022 x 10²³ iron atoms (i.e. 1 mole of iron) have a mass of **55.845 grams**

70

Practice

The symbol for "mole" is "mol"

- Not much shorter than "mole"
- But it allows us to use the singular form just as with the symbols for meter or gram.

1.5 mole or 1.5 moles? 0.75 mole or moles?

We just say: 1.5 mol 0.75 mol

The concept of "mole" and molar mass

Calculate the number of iron atoms in a 4.48 mol sample of iron.

PracticeWhich of the following is closest to the average mass of one atom of copper?a) 63.55 g

The concept of "mole" and molar mass

- b) 52.00 g
- c) 58.93 g
- d) 65.38 g
- e) 1.055×10^{-22} g

73

Practice Which of the fol greatest numbe	lowing 100 r of atoms).0-g sample ?	s contains the
a) Magnesium e) Same for all	b) Zinc	c) Silver	d) Calcium

74

The concept of "mole" and molar mass How many C atoms in 1 mole of Carbon? How many O₂ molecules in 1 mole of Oxygen gas? How many O <u>atoms</u> in 1 mole of Oxygen gas? How many formula units in 1 mole of CaCl₂? How many Cl atoms in 1 mole of CaCl₂? What is the mass of 1 mole of Carbon? What is the mass of 1 mole of Oxygen gas? What is the mass of 1 mole of CaCl₂?

75





The element rhenium (Re) exists as 2 stable isotopes and 18 unstable isotopes. The nucleus of rhenium-185 contains:

- a) 75 protons and 75 neutrons
- b) 75 protons and 130 neutrons
- c) 130 protons and 75 neutrons
- d) 75 protons and 110 neutrons

Which of the following statements are true?

- I. The number of protons is the same for all neutral atoms of an element.
- II. The number of electrons is the same for all neutral atoms of an element.
- III. The number of neutrons is the same for all neutral atoms of an element.
- a) I, II, and III are true
- b) Only I and II are true
- c) Only II and III are true
- d) Only I and III are true
- e) I, II, and III are false.

79

LonsCations• Formed when an atom loses one or more electrons $Li \rightarrow Li^+ + e^-$
 $Ba \rightarrow Ba^{2+} + 2e^-$ Anions• Formed when an atom gains one or more electrons $F + e^- \rightarrow F^-$
 $N + 3e^- \rightarrow N^{3-}$

Note that we put the size of the charge before the sign: 2+ instead of +2 3- instead of -3

80

lons

Unless the atom is undergoing a nuclear reaction (which is not chemistry), ions are formed only by gaining or losing electrons lons are denoted by a superscript on the right side of the entity, indicating the charge.

Examples:

$$Cl^ Ca^{2+}$$
 S^2

81



How is an ion formed in a chemical process, starting with a neutral atom?

- a) By adding or removing protons
- b) By adding or removing electrons
- c) By adding or removing neutrons
- d) All of these are true
- e) Two of these are true.





Periods are horizontal																	
	1 H		Period 1														
	3 Li	4 Be							Period 2			5 B	° C) N	8 O	9 F	10 Ne
	II Na	12 Mg							Period 3			D 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		Period 4	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	37 Rb	38 Sr	39 Y	40 Z.r	41 Nb	42 Mo	43 Te		Period 5	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	24 W	75 Re	,	Period 6	79 Au	80 Hg	81 TI	82 РЪ	83 Bi	84 Po	ss At	so Rn
	87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh		Period 7	III Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
																	-

87



The Periodic Table

Periods

- horizontal rows of elements
- properties change in a similar way in each period
- with each new period, the trend repeats (or more like "rhymes")

Groups or Families

- elements in the same vertical columns
- have similar chemical properties

Most elements are metals

Nonmetals are huddled towards the top-right corner

86





Groups or "Families" of elements and their ions

- Metals form cations by losing electrons
- Main group metals lose as many electrons as their main group number

cation charge = main group

- Nonmetals form anions by gaining electrons
- Nonmetal anion charge size is the difference between main group number and 8 (main group number of noble gases at the very right)

anion charge = {main group #} - 8