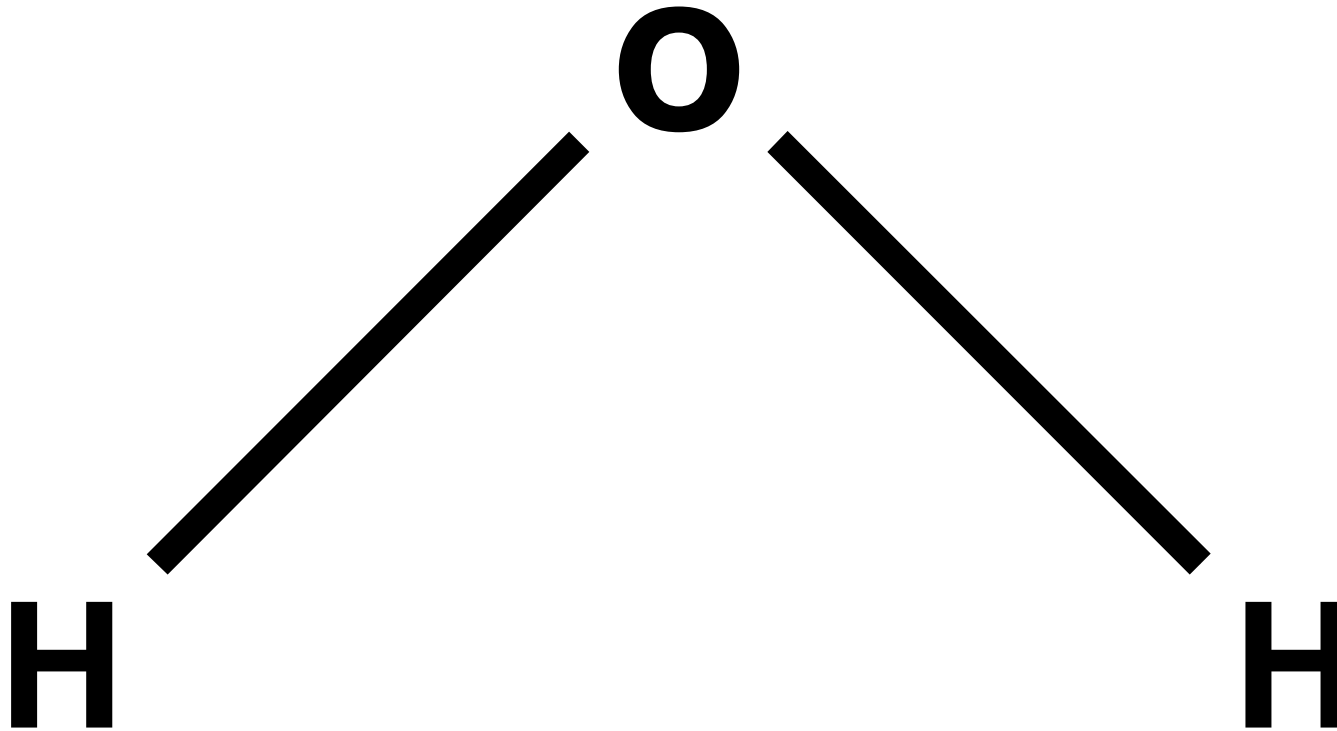


C1403 Lecture 3, Wednesday, September 14, 2005



Water

**Water, water, everywhere,
Nor any drop to drink.**

**Samuel Taylor Coleridge,
The Rime of the Ancient Mariner, 1798.**

If there is magic on this planet, it is contained in water....

Its substance reaches everywhere; it touches the past and prepares the future;

it moves under the poles and wanders thinly in the heights of the air;

It can assume forms of exquisite perfection in a snowflake,

or strip the living to a single shining bone cast up by the sea.

**Loren Eiseley
(Anthropologist)**

Structure: an intellectual technique to answer questions concerning the makeup of matter and light

Mathematical structure from geometry

Composition: number and kinds of elements in a set

Constitution: connections between the elements of a set

Configuration: position of the connected elements in 3 D

Application of mathematical structure to chemistry:

Let mathematical "elements" = atoms, then

Composition: What numbers and kinds of atoms?

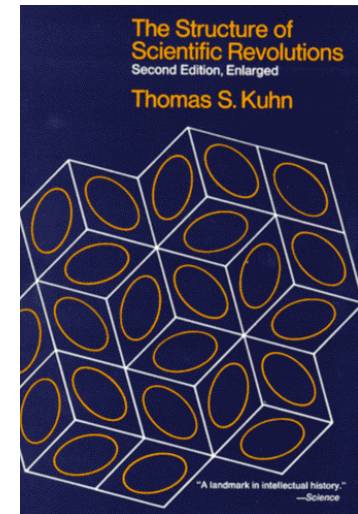
Constitution: How are the atoms connected?

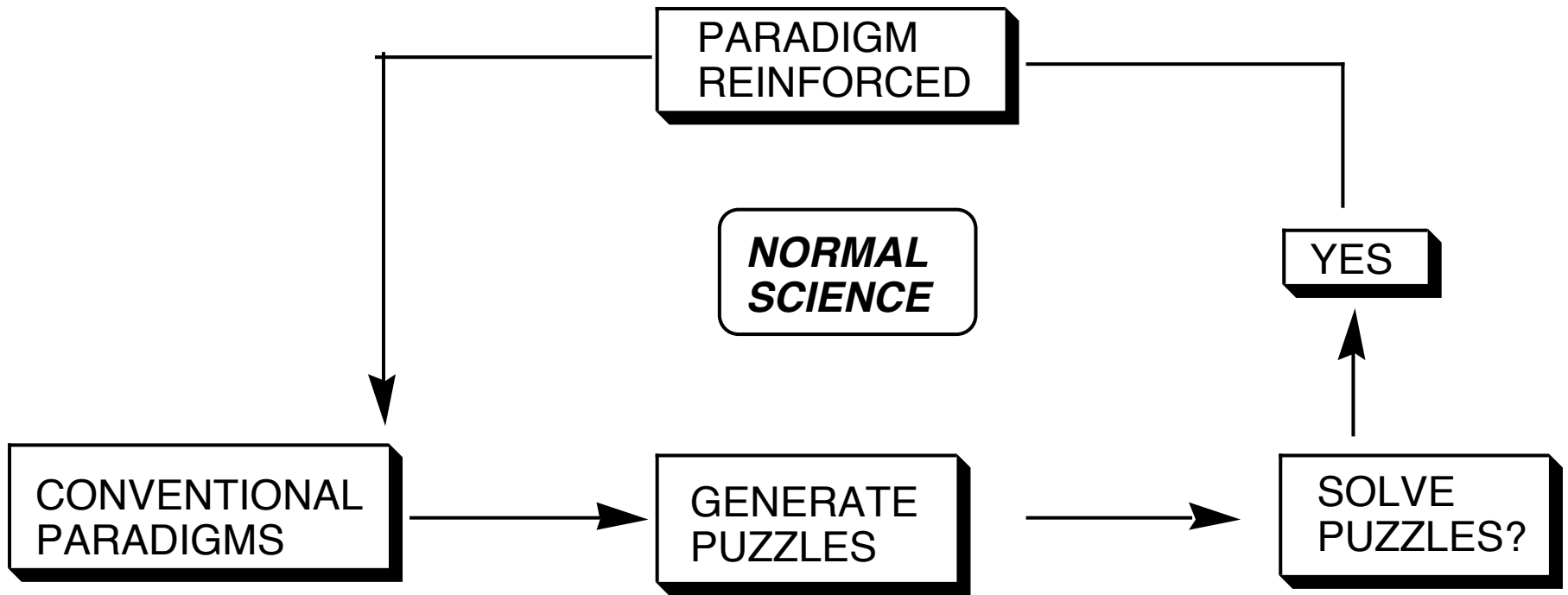
Configuration: How are the atoms positioned in space?



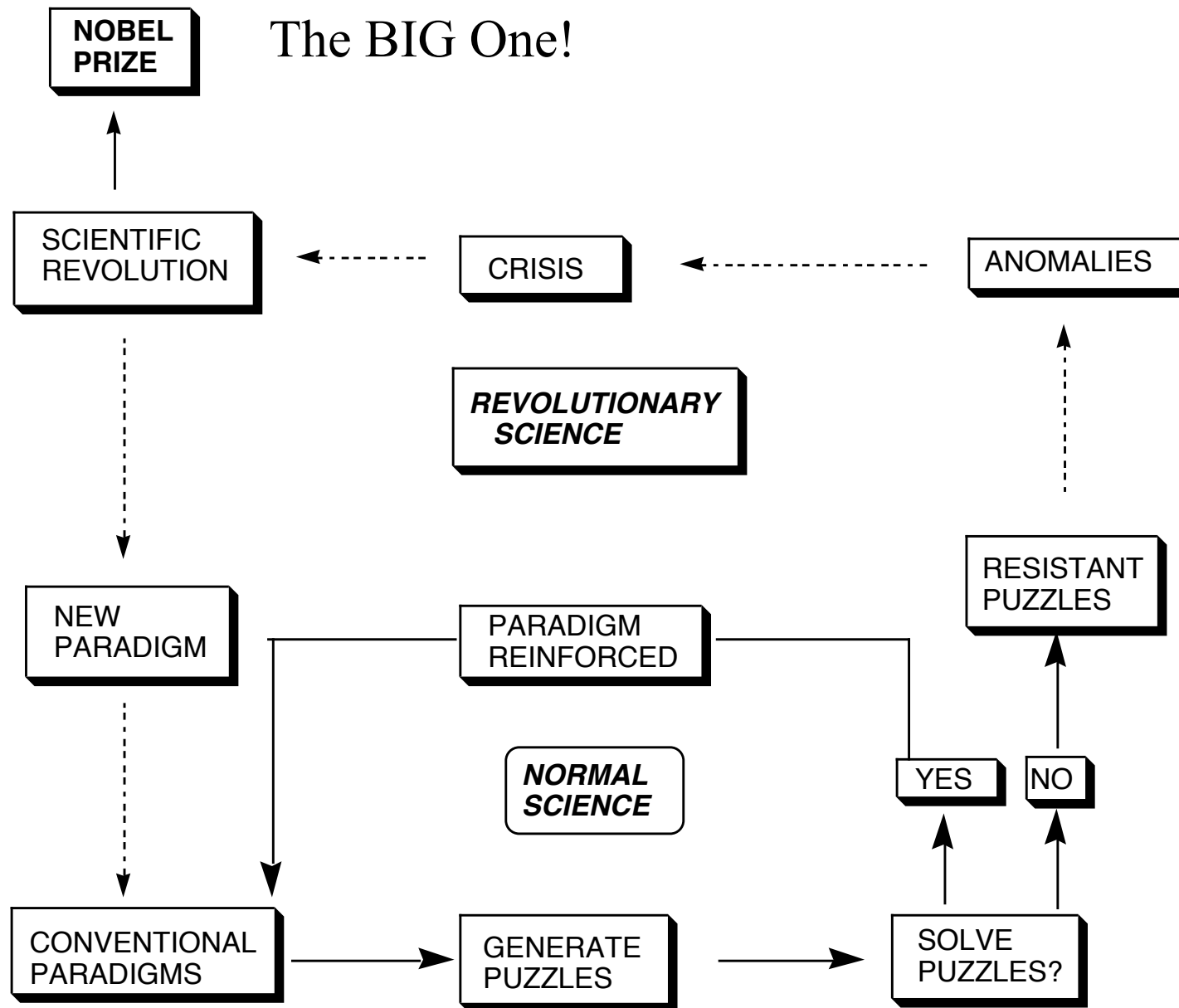
Thomas Kuhn. 1923-1996.

Paradigm: A characteristic set of beliefs and/or preconceptions (theoretical, instrumental, procedural and metaphysical) that is shared by a community of practitioners. In a global sense the paradigm embraces all of the shared commitments of a scientific group. A paradigm is what defines the scientific community.

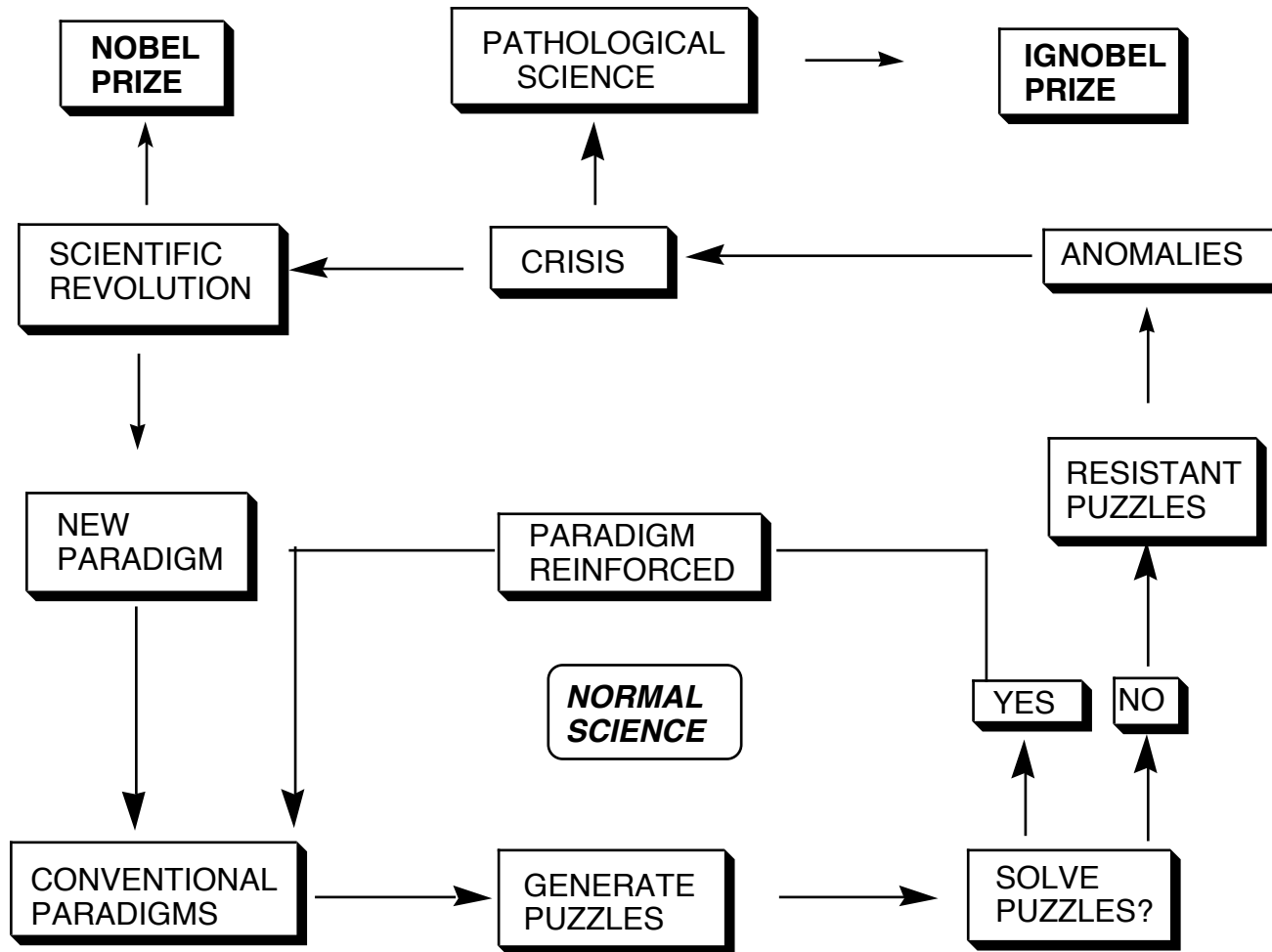




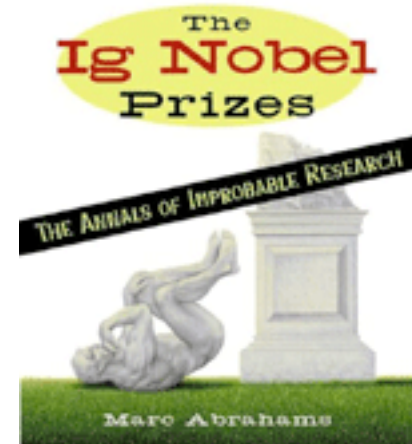
Flow diagram for normal science: This is how text books describe science.



Flow diagram for revolutionary science: Extraordinary claims that become accepted and are integrated into “normal science.”



Nobel Prize?



Ig Nobel Prize?

**Flow diagram for pathological and revolutionary science.
Will an extraordinary claim become Nobel or Ig Nobel science?**



H. Kolbe

1818-1884

"In a recently published paper, I pointed out that one of the causes of the present regression of chemical research in Germany is the lack of general, and at the same time thorough chemical knowledge; no small number of our professors of chemistry, with great harm to our science, are laboring under this lack. A consequence of this is the spread of the weed of the apparently scholarly and clever, but actually trivial and stupid, natural philosophy, which was displaced fifty years ago by exact science, but which is now brought forth again, out of the store room harboring the errors of the human mind; by pseudoscientists who try to smuggle it, like a fashionably dressed and freshly rouged prostitute, into good society, where it does not belong."

H. Kolbe, "A Sign of the Times"
J. Prakt. Chem., **15**, 474 (1877).



J. H. van't Hoff
(1852-1911)
First Nobel Prize,
Chemistry, 1901

“A Dr. J. H. van't Hoff, of the Veterinary School at Utrecht, has no liking, apparently, for exact chemical investigation. He has considered it more comfortable to mount Pegasus (apparently borrowed from the Veterinary School) and to proclaim in his book how the atoms appear to him to be arranged in space, when he is on the chemical Mt. Parnassus which he has reached by bold flight.”

H. Kolbe, “A Sign of the Times
J. Prakt. Chem., **15**, 474 (1877).

Chapters 1- 2 Stoichiometry: Some Learning Goals

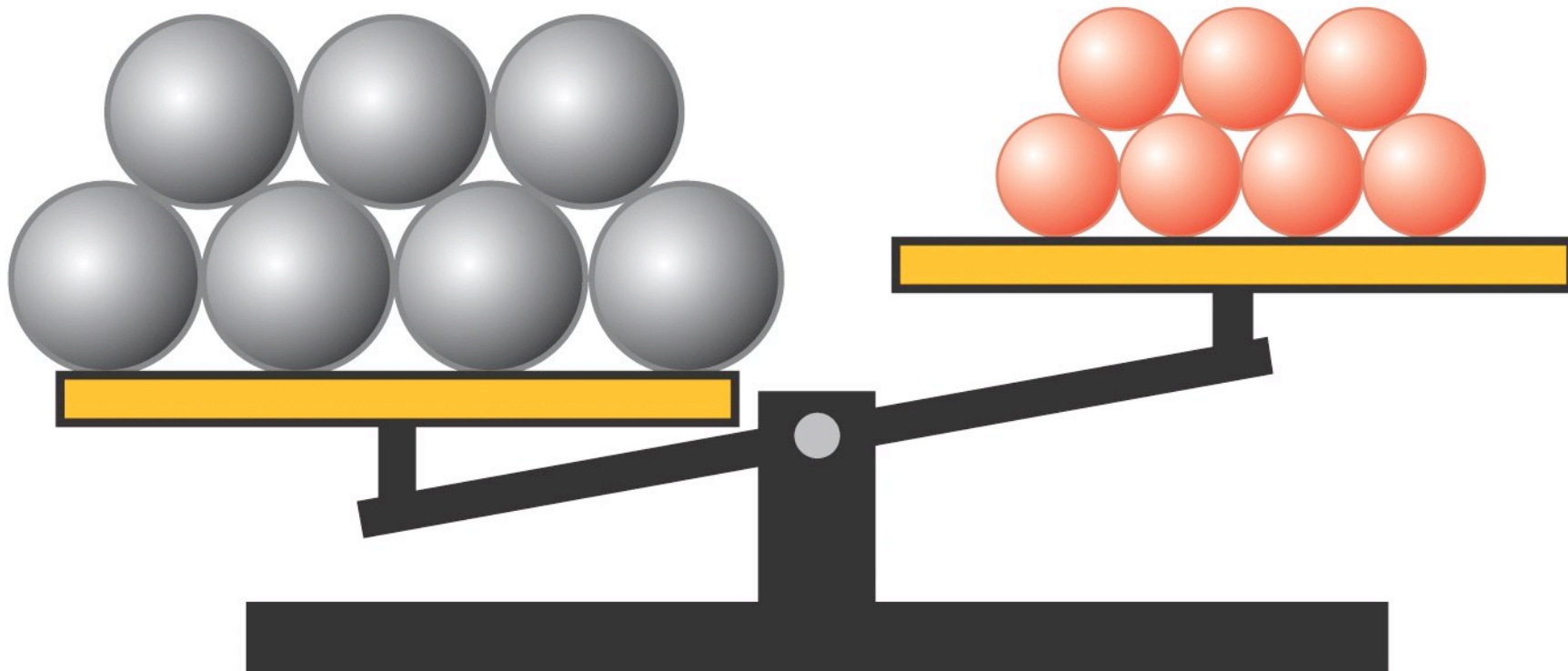
Stoichiometry: the science dealing with quantitative relationships involving the mass of substances and the number of particles. Counting atoms by weighing.

Chapter 1 (substances in isolation; elements and compounds)

- (1) Mole Concept: Convert mass to moles and moles to mass (1-7)
- (2) Molecular formulas from Avogadro's hypothesis
- (3) Compute % elements in compounds (1-8)
- (4) Distinguish between empirical and molecular formulae (1-8)
- (5) Compute empirical formulas (1-8)

Chapter 2 (substances in action: chemical reaction)

- (6) Balance chemical equations (2-1)
- (7) Mass (mole) relationships for chemical reactions (2-2)
- (8) Limiting reagent in chemical reactions (2-3)



Equal amounts

The *mole concept*: In chemistry equal amounts refer to equal *numbers (moles)*, not equal *weights (grams)*. BUT, moles = numbers = weight

(2) Molecular formulas from Avogadro's hypothesis

The Law of Combining Volumes of Gases: When two gases react, the volumes that combine are in a ratio of small whole numbers. The ratio of the volume of each product, if a gas, is also in the ratio of small whole numbers.

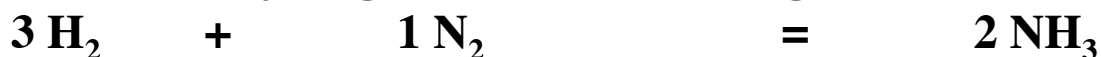
1 Liter of hydrogen + 1 Liter of chlorine = 2 Liters of hydrogen chloride



2 Liters of hydrogen + 1 Liter of oxygen = 2 Liters of Water



3 Liters of hydrogen + 1 Liter of nitrogen = 2 Liters of Ammonia



Mass is always conserved; but the volume of a gas is not.

Avogadro's Law: Equal volumes of different gases contain the same number of *particles*. The particles of a gas may be atoms or molecules. One liter of hydrogen = one liter of chlorine = one liter of hydrogen chloride in terms of particles (read molecules)

*From empirical formulas to molecular formulas through
Avogadro's hypothesis and the densities of gases*

Equal volumes of different gases contain the same number of particles (atoms or molecules).

Logic: If equal volumes contain equal numbers of particles, the ratio of the *masses of equal volumes* is the same as the *ratio of the masses of the particles*.

Thus, with the selection of a standard “particle”, the masses of equal volumes of gases provides a simple basis for establishing atomic and molecular weights.

The substance hydrogen (molecular weight = 2) was selected as the standard.

Hydrogen as a standard for molecular weights

With H₂ (MW = 2 g) as the standard, *the molecular weight is given by the density of the gas times the volume of a mole of the gas (22.4 L).*

$$\text{Molecular weight} = \text{density (gL}^{-1}\text{)} \times 22.4 \text{ L}$$

Example:

$$\text{Density of hydrogen gas} = 0.090 \text{ gL}^{-1}$$

$$\text{MW of hydrogen defined as 2 (H}_2\text{), i.e., MW (H}_2\text{)} = 0.090 \text{ gL}^{-1} \times 22.4 \text{ L} = 2.0 \text{ g}$$

On the hydrogen scale the weight of one mole (6×10^{23}) of some important atoms:

H	=	1 g
C	=	12 g
N	=	14 g
O	=	16 g
F	=	19 g

On this scale the weight of one mole (6×10^{23}) of some important small molecules:

H ₂	=	2g
H ₂ O	=	18 g
CO ₂	=	44 g
N ₂	=	28 g
O ₂	=	32 g
CO	=	28 g

These atomic and molecular weights are different but *the number of atoms or molecules are the same.*

Computing the molecular weight of gases from densities
Exemplars: oxygen and ozone

Problem: density of oxygen gas (O_2) = 1.43 gL^{-1} . What is the MW of oxygen “particles” in the gas?

Answer: MW of oxygen particles is $1.43 \text{ gL}^{-1} \times 22.4 \text{ L} = 32 \text{ g}$

Problem: density of ozone gas (O_3) is 2.14 gL^{-1} . What is the molecular weight of ozone?

Answer: MW of ozone particles is $2.14 \text{ gL}^{-1} \times 22.4 \text{ L} = 48 \text{ g}$

These data are all consistent with the AW of hydrogen atoms = 1 g, the AW of oxygen atoms = 16 g and the MW of hydrogen (H_2) gas = 2 g, the MW of oxygen (O_2) gas = 32 g and the MW of ozone (O_3) gas = 48 g.

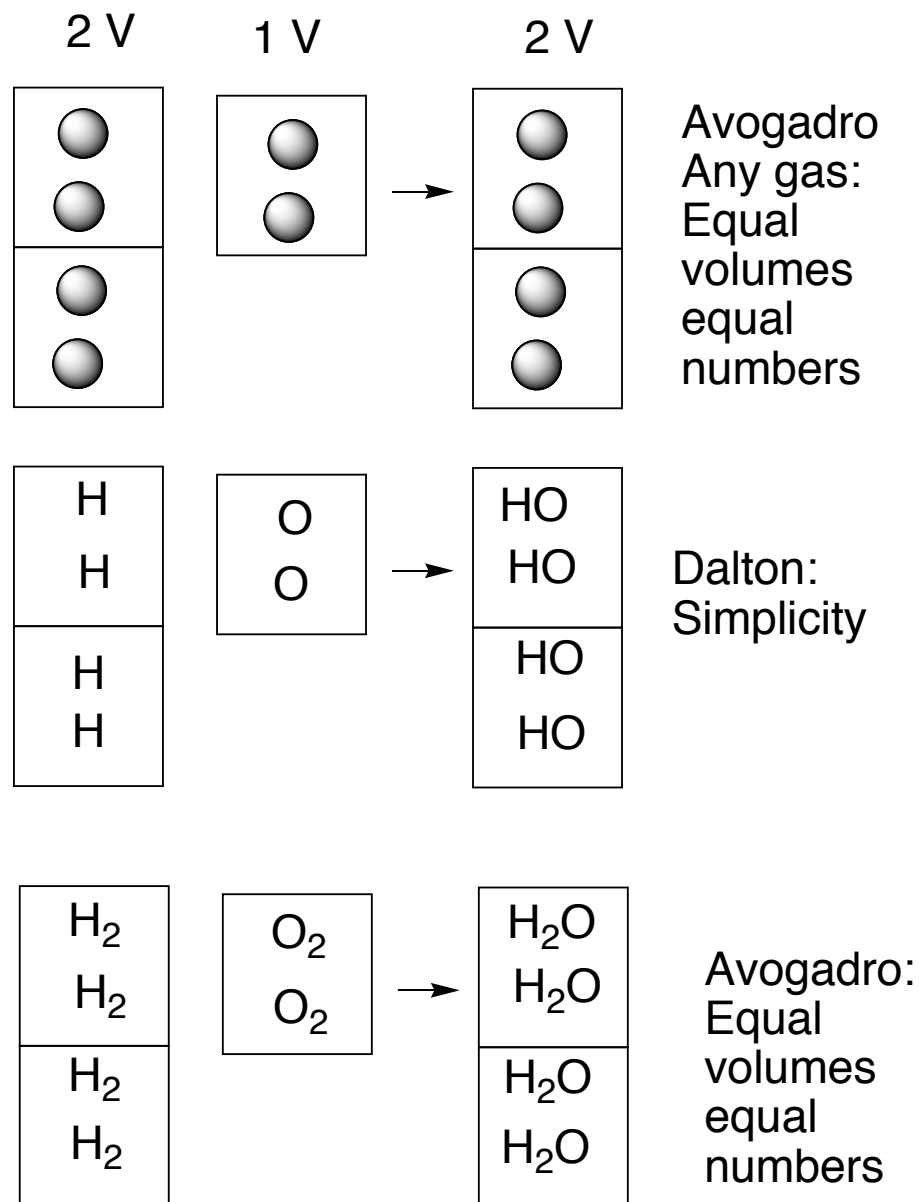
Science as the battleground of ideas.
 May the best paradigm win!

Dalton: The composition of all gaseous elements are single atoms (simplicity):
 $H + O = HO$

Avogadro: The composition of gaseous elements are diatomic molecules (equal volumes equal particles):
 $2H_2 + O_2 = 2H_2O$

Cannizzaro: Use Avogadro's hypothesis and show that a consistent set of atomic and molecular weights could be created by just using Avogadro's hypothesis and no further assumptions. Dalton's hypothesis does not work.

Avogadro's paradigm wins! (Not Avogadro!!)



Perform calculations employing the mole (the chemical amount) concept.

Counting atoms and molecules in a mole of a compound.

How many water molecules in 18 g of water (H_2O)?

Compute MW of water first: Since AW of H = 1 and AW of O is 16, the molecular weight of H_2O is 18, so one mole of water weights 18 g, which contains 6×10^{23} molecules of water.

How many hydrogen atoms in 18 g of water?

Each mole of water contains 2 hydrogen atoms, so one mole of water contains $2 \times 6 \times 10^{23}$ molecules (two moles) of hydrogen atoms.

How many oxygen atoms in 18 g of water?

Each mole of water contains 1 oxygen atom, so one mole of water contains 6×10^{23} molecules (one mole) of oxygen atoms.

(3) Computing % composition from an empirical or molecular formula of a compound

Strategy: From the empirical or molecular formula compute the mass of each element in one mole of the compound (need molecular formula to do this). Add the atomic molar masses to compute the mass of one mole of the compound. Divide each atomic mass by the mass of one mole of the compound to obtain the % of each element in the compound.

Exemplar: Compute the composition of hydrogen and oxygen in water.

The composition of water is H_2O .

The atomic wt of H is 1 and the atomic wt of O is 16, so the wt of one mole of water is 18 g.

The percent compositions of the elements in water is:

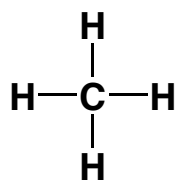
$$\% \text{ H} = 2\text{g}/18\text{g} \times 100\% = 11.1; \quad \% \text{ O} = 16\text{g}/18\text{g} \times 100\% = 88.9 \%$$

(4) Distinguish between empirical formula, molecular formula, structural formula.

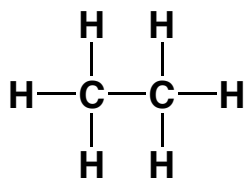
Empirical formula: a compositional formula that shows the relative number and kinds of atoms in the smallest whole numbers in a molecule. Exemplars: empirical formula, CH_2 . This is the empirical formula for C_2H_4 (ethylene), C_3H_6 (propene), or C_4H_8 (butene)

Molecular formula: a compositional formula that shows the actual number and kinds of atoms in a molecule. Exemplars: C_2H_4 (ethylene), C_3H_6 (propene), or C_4H_8 (butene)

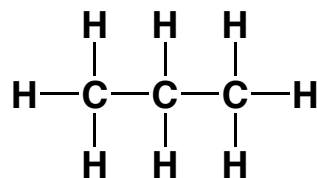
Molecular structural (constitutional) formula: a formula that shows not only the numbers and kinds of atoms in a molecule, but also shows how the atoms are connected to one another. Exemplars:



methane



ethane



propane

(5) Computing an empirical formula from an elemental analysis

Strategy: Starting from the experimental wts of the elements from an elemental analysis of a sample of a compound, compute the number of moles of each of the elements in the sample, using the periodic table for the values of atomic masses. The numbers of moles of each element computed are directly related to the *relative* numbers of atoms in a molecule of the compound.

Exemplar: An elemental analysis of 100 g of water provided the following values: H = 11.1 g and O = 88.9 g.

Converting to moles: 11.1 g of H = $11.1/1 = 11.1$ mol and 88.8 g of O = $88.9/16 = 5.56$ mol.

The ratio $H/O = 11.1/5.56 = 2$. The empirical (simplest) formula of water is H_2O . The results are also consistent with H_4O_2 , H_6O_3 , etc.

(5) Computation of the empirical formulas for three hydrogen oxides.

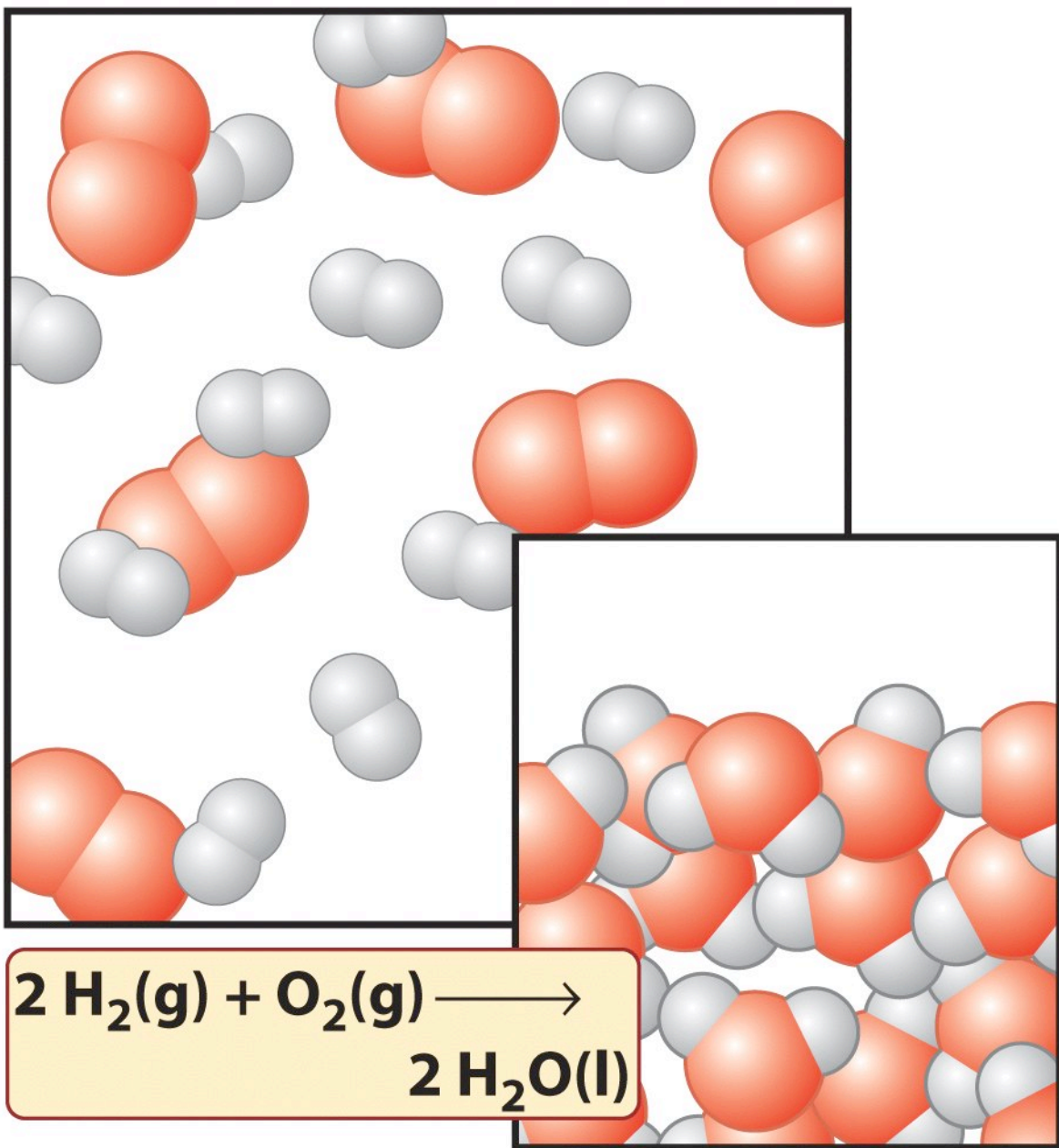
- (1) Assume a sample of 100 g for the computation (any mass will work, but selecting 100 makes the computation straightforward)**
- (2) Translate the % mass into g (Example: Suppose O is 89% of the total mass of a substance. For a 100 g sample of the substance, the sample contains 89 g of O).**
- (3) Compute the number of mol of each element in the 100 g sample by dividing the mass of the element in the sample by the atomic weight of the element (H = 1, O = 16).**
- (4) The ratio of the molar masses of the elements in the substance is directly proportional (within round off error) to the ratio of the atoms in the substance.**
- (5) Express the number of mol of each element in a chemical formula using the smallest possible whole numbers.**

Common Name	%H	%O	Moles H in 100 g of substance	Moles O in 100g	Molar Ratio H/O	Empirical Formula	Molecular Formula
Water	11%	89%	11 mol (11g/1gmol ⁻¹)	5.6 mol (89g/16 gmol ⁻¹)	1.95 ~ 2/1	H ₂ O	H ₂ O
Hydrogen Peroxide	6.0%	94%	6.0 mol (6g/1 gmol ⁻¹)	5.9 mol (94g/16 gmol ⁻¹)	1.01 ~ 1/1	HO	H ₂ O ₂
Hydrogen Trioxide	4.0%	96%	4.0 mol (4g/1 gmol ⁻¹)	6.0 mol (96g/16 gmol ⁻¹)	.67 ~ 2/3	H ₂ O ₃	H ₂ O ₃

(5) Computation of the empirical formulas for four nitrogen oxides.

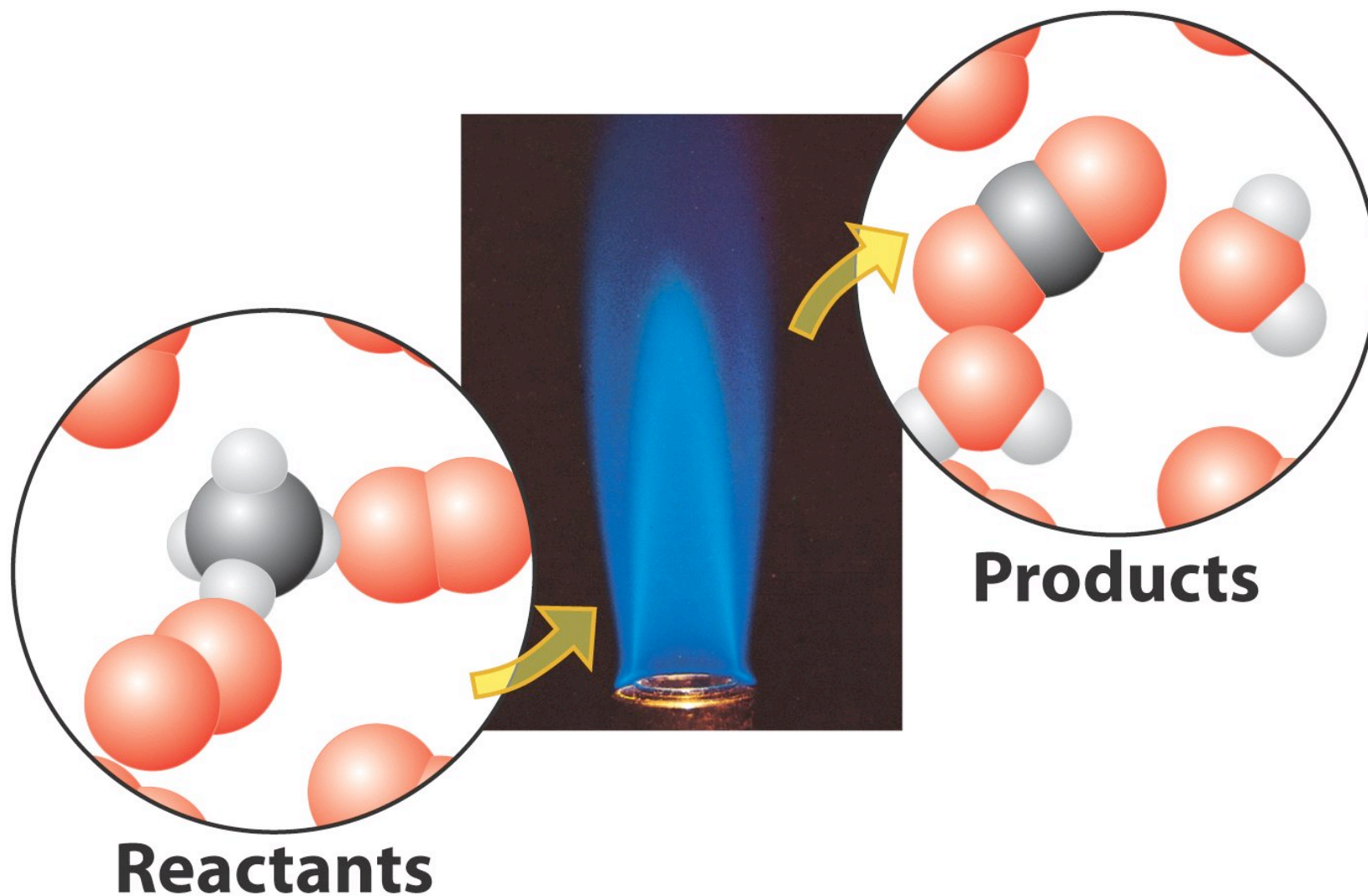
- (1) Assume a sample of 100 g for the computation (any mass will work, but selecting 100 makes the computation straightforward)**
- (2) Translate the % mass into g (Example: Suppose N is 47% of the total mass of a substance. For a 100 g sample of the substance, the sample contains 47 g of N).**
- (3) Compute the number of mol of each element in the 100 g sample by dividing the mass of the element in the sample by the atomic weight of the element.**
- (4) The ratio of the molar masses of the elements in the substance is directly proportional (within round off error) to the ratio of the atoms in the substance.**
- (5) Express the number of mol of each element in a chemical formula using the smallest possible whole numbers.**

Common Name	%N	%O	Moles N in 100 g of substance	Moles O in 100g	Molar Ratio N/O	Empirical Formula	Molecular Formula
Nitric Oxide	47%	53%	3.4 (47g/14gmol ⁻¹)	3.3 (53g/16 gmol ⁻¹)	1.03 ~ 1/1	NO	NO
Nitrous Oxide	64%	36%	4.6 (64g/14 gmol ⁻¹)	2.3 (36g/16 gmol ⁻¹)	2.0 ~ 2/1	N ₂ O	N ₂ O
Nitrogen Dioxide	30%	70%	2.1 (30g/14 gmol ⁻¹)	4.4 (70g/16 gmol ⁻¹)	0.48 ~ 1/2	NO ₂	NO ₂
Dinitrogen Dioxide	47%	53%	3.4 (47g/14 gmol ⁻¹)	3.3 (53g/16 gmol ⁻¹)	1.03 ~ 1/1	NO	N ₂ O ₂



Atomic and molecular visualization of the reaction of hydrogen and oxygen to form water.

Burning hydrocarbons: $? C_xH_y + ? O_2 = ? CO_2 + ? H_2O$



(6) *Balancing chemical equations*

Chemical equations: An algebraic representation of a chemical reaction.

Balanced chemical equation: Number of moles of atoms on each side of the equation are identical (*Law of conservation of atoms in a chemical reaction*).

Balancing a chemical equation that describes a reaction involves inserting coefficients before the chemical formulas so that the same number of each type of atom is shown on each side of the equation.

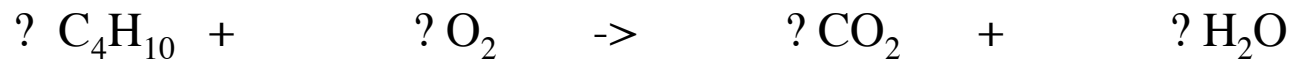
Chemical equations may be balanced "by inspection" or algebraically (Section 2.1, pages 55-57). Inspection is the preferred way for simple reactions.

(6) Strategy for balancing chemical equations:

- (a) Start by giving the coefficient 1 to the **most complex formula**.
(The one that contains the most different elements).
- (b) Inspect both sides of the equation for elements that appear in only one formula which the coefficient is unassigned and balance for that element.
- (c) Repeat balancing elements, until all are balanced.
- (d) By convention, balanced equations have only integer coefficients. Eliminate fractional coefficients by multiplying all the formulae by the smallest integer that eliminates the fraction.

Using balanced chemical equations (2.2)

Combustion of a hydrocarbon (compounds that contain C and H atoms only):



Select most complex formula and assign coefficient = 1.



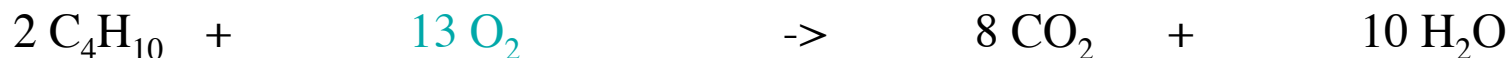
For remaining formulae, give coefficients to those that only appear once in equation.



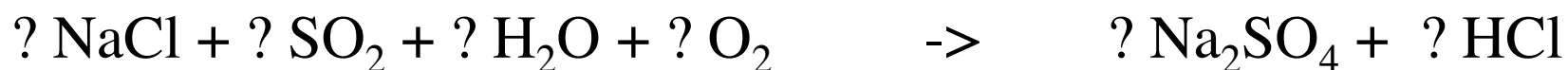
Complete assignment of coefficients.



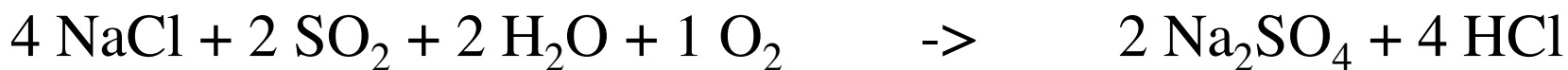
Get rid of any fractions:



Example: Find whole numbers for the ? which balance atoms.



Balanced Equation (remove fractional coefficients):

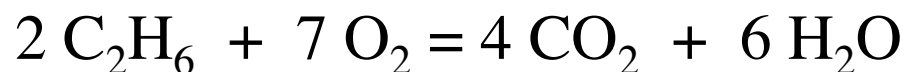


(8) Limiting reactants

If reactants are mixed in random amounts, generally one of them will be used up first and at that point, the reaction stops dead (no more atoms of that reactant!).

The reactant that is used up first in a chemical reaction is termed the limiting reactant.

Example: combustion of a hydrocarbon.



The limiting reactant is identified as follows:

(1) A product is selected (any product will do).

(2) The balanced equation is used to compute the amount of product that would be produced from the available supply (weight) of each reactant.

(3) *The reactant which gives the smallest yield of product is the limiting reactant.*

(8) Example of a limiting reactant problem:

Balanced Equation: $2 \text{C}_2\text{H}_6 + 7 \text{O}_2 = 4 \text{CO}_2 + 6 \text{H}_2\text{O}$

Pick CO_2 as the product whose yield is to be computed.

Suppose the amounts of reactants: 15 g of C_2H_6 and 224 g of O_2

Which gives the smallest yield of CO_2 ?

15 g / 15 g mol⁻¹ of $\text{C}_2\text{H}_6 = 1$ mole; yield of $\text{CO}_2 = 2$ moles of CO_2

224 g / 32 g mol⁻¹ of $\text{O}_2 = 7$ moles; yield of $\text{CO}_2 = 4$ moles of CO_2

Limiting reactant is C_2H_6 . 1 mole of C_2H_6 (15 g) reacts with 3.5 mole of O_2 (112 g) and the reaction stops. 3.5 moles of O_2 (112 g) are left in excess.

From empirical formula to molecular weight
Another exemplar

Problem: A hydrocarbon gas has an empirical formula of CH. The gas has a density of 1.16 gL^{-1} . What is the molecular weight of the gas?

Answer:

- (1) We symbolize the molecular formula as $(\text{CH})_n$. We need to solve for n.
- (2) The MW of the hydrocarbon gas is given by the density of the gas time the molar volume: $\text{MW} = 1.16 \text{ gL}^{-1} \times 22.4 \text{ L} = 26 \text{ g}$.
- (3) The empirical formula CH corresponds to an atomic mass of 13. Dividing this empirical weight into the molecular weight gives the multiplier that takes the empirical formula into the molecular formula: $26/13 = 2$.
- (4) Thus, $n = 2$ so that $(\text{CH})_n$ becomes $(\text{CH})_2$ or written in the accepted way for a molecular formula or molecular composition: C_2H_2 .
- (5) There is only one substance with the composition C_2H_2 . That substance is acetylene whose molecular structure is