

How "X" got its chemical identity

Summary

Many of us and our students face difficulty in learning atomic theory and understanding molecular formulae. On one level, we can see it as a problem of memorization, or of learning a new language (of chemistry) with a new set of symbols. But actually the problem is not just of the new symbols but lies much deeper. The formulae are more than a set of facts to be memorized. These are conclusions derived from results of experiments done over decades, for each substance, by a large number of scientists. These scientists sometimes helped each other, and sometimes even opposed or fought with each other. On one hand, these experimental details show that the notion of chemical formulae is a result of human thought process and dynamics. On the other hand, the knowledge of these experiments prepares us to understand subsequent changes in the disciplines of modern science. A historical study can be of profound help in teaching-learning of this dimension of science.

This unit walks through some of the historical developments that contributed to the establishment of molecular formula of a liquid substance. The developments were sometimes *experimental findings* and sometimes new *theoretical assumptions* which contributed to building up of modern atomic theory. The unit consists of passages containing historical information and problems of logical inconsistencies that arose with these developments, followed by a set of questions. The students are expected to answer the questions based on information provided prior to the question only (and not what they might already know or have studied in their science textbooks). It is important that students go through the unit in sequential manner, which will help them learn construction of logic and theory.

Minimum Time required: 4 sessions of 40 min

Type of LU: Classroom

Material required: Only this worksheet and a pen/pencil.

Links to Curriculum: NCERT Class 9 Science textbook:

- Chapter 2: Is matter around us pure
- Chapter 3: Atoms and Molecules
- Chapter 4: Structure of the Atom

Learning Objectives:

- 1) To see an example of how mass and volume measurements of gases played a big role in development of modern chemical theory of substances.
- 2) To be able to differentiate between experimental results, assumptions and conclusions.
- 3) To realize that molecular formula of a substance is not an ever-known fact but a conclusion derived based on certain assumptions and certain experimental findings. A change in assumptions or theoretical framework may change this.

- 4) To learn why some of the ideas that were proposed alternate to modern atomic theory were not taken forward in modern science.
- 5) To understand that analysis of historical information from multiple perspectives can be a useful tool to understand modern scientific theories/knowledge.

Introduction

In Science, many substances are represented using molecular formulae, which also provide the chemical description for those substances. Molecular formulae contain some alphabetical symbols and some numbers written at a lower level than the alphabets. For example, mercury is represented as Hg, water as H_2O , lime as CaO , cane sugar as $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. For many substances, the origin of these alphabets and numbers has a long history.

In this Learning Unit, we will look at where the numbers in the molecular formula of one such substance came from. This became possible only after technologies developed for (i) mass and volume measurements of gases (ii) controlling temperature and pressure of these gases, and (iii) controlled use of electricity. For gases reacting with each other, mass and volume measurements gave very puzzling results. This unit presents some of those results. Then it shows how by imagining some models of atoms (unit particles of solids, liquids and gases) and making some assumptions about them, those puzzles were solved.

Tasks in this Learning Unit consist of reading two kinds of paragraphs, along with associated questions.

I. 'Into the past': These sections describe the experiments or theoretical developments that took place about 2 centuries ago.

II. 'Playing with the results': In these sections, you will explore different ways to interpret or represent the experimental results and theoretical ideas.

By the end of this unit, we will be able to see that the chemical formulae used in science have evolved from experimental findings, theories and certain assumptions.

Task 1: The "X"

Into the past...

For ages, there was a liquid substance which everyone had seen but no one knew what it is made of. Some said it was one of the purest substances of nature and had nothing else in it. Many people tried decomposing (breaking it down) into components but were unsuccessful. Even heating it to high temperatures did not break it into components but converted it to an invisible form. People in different countries called it by different names. We will call it X.

In 1777, a chemistry professor in France, Mr. Macquer was burning a gas in air. He saw a strange phenomena. On a dish held above the burning gas, a liquid was being formed on its lower surface. Let us call this burning gas "A". Mr. John Warltire in England also observed the same phenomena. Four years later, an English priest, Dr. Priestly observed the same phenomena again. He wondered if this liquid was X and if it was being produced by burning of gas A or coming from some other source. So he told it to his friends. At least three persons in Europe found this observation new and did experiments on it as described in Figure 2— Mr. Cavendish (a physicist in England), Mr. James Watt (an Engineer in Scotland), and Mr. Antoine Lavoisier (a tax collector and scientist in France).

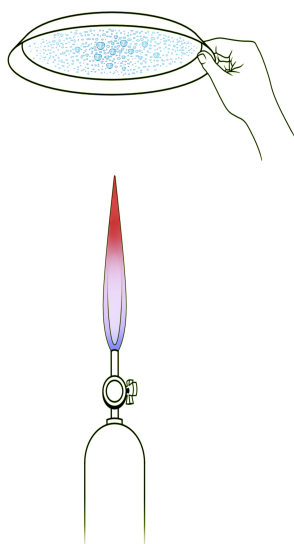


Figure 1: Mr. Macquer's experiment

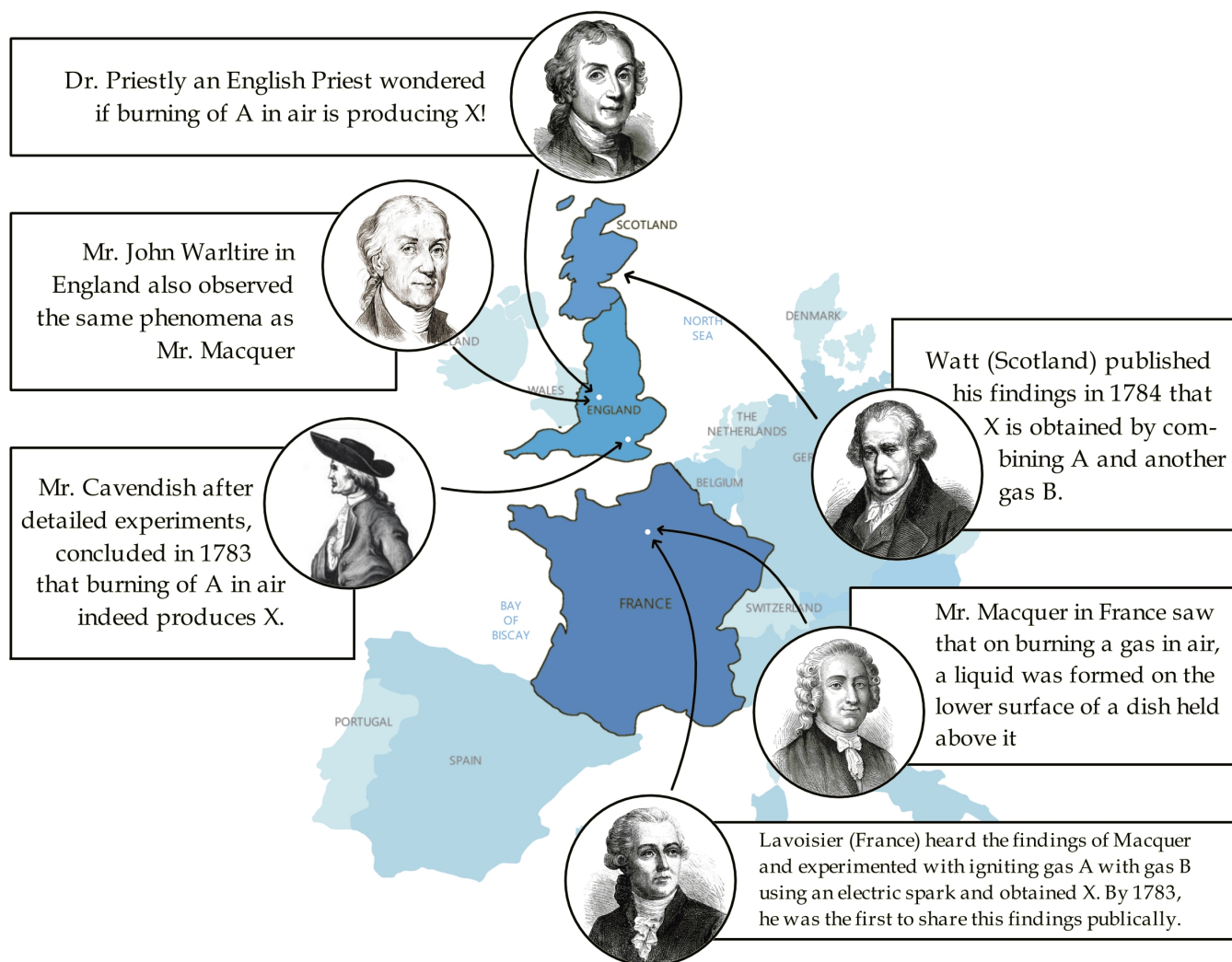


Figure 2: Experiments done by various people across Europe

Q1. What were the differences and similarities between the findings by Mr. Lavoisier, Mr. Watt, and Mr. Cavendish mentioned in figure above?

The experiments done by the three scientists were different. Henry Cavendish burned **A** in air, James Watt combined **A** and **B** (probably also by burning), whereas Antoine Lavoisier mixed **A** and **B** and ignited with a spark. Hence, James Watt and Lavoisier were familiar with the role of gas **B** in forming **X**. They all found that the substance formed was indeed the substance **X**.

Mr. Lavoisier also measured the mass of **X** formed and found it to be same as the sum of masses of **A** and **B** used.

Around that time, many scientists had found a new kind of energy which could decompose (break down) liquids, they called it electricity. By 1800, Mr. Alessandro Volta managed to produce an electricity source by piling up zinc and silver discs. Immediately, an English surgeon Mr. Anthony Carlisle and his colleague Mr. William Nicholson used this electric source and showed that "**X**" in liquid state could also be broken down into the two substances "**A**" and "**B**".

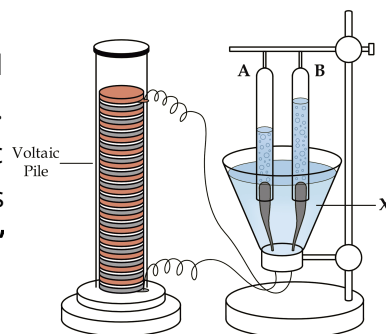


Figure 3: Experimental set-up for electrolysis.

Q2. What new did this electrolysis experiment show about **X** which Lavoisier's experiment didn't?

Electrolysis of **X** was successfully done by several people before 1800 also, but the earlier attempts could not obtain 2 separate gases from it. Moreover, getting back only **A** and **B** from **X** and the mass equivalence established that **X** consists of **A** and **B** only, and nothing else.

Playing with the results...

Thus, experiments done by many people in many countries together established that **X** was not an element but _____.(**Complete the sentence**)

Let students write whatever they think about **X**. Do not insist on writing that it was a compound, because so far we have not mentioned about fixed proportion of **A** and **B** in **X**. Even if students say it to be a mixture, it is acceptable for this task. Most important at this stage is that they should realize that **X** contains (only) **A** and **B**.

Task 2: The Mystery of Mass Ratio: The Concept of Atoms

Back to the past...

Mr. Cavendish made more accurate mass measurements than Mr. Lavoisier. These, and later improved experiments found that **X** always had about 11% **A** and 89% **B** by mass.

Q1. Calculate the ratio of mass of **A** to mass of **B** in **X** in terms of approximate smallest whole numbers.

1:8; Students may divide 89 by 11 and get a fractional number. It is important to discuss here that Cavendish was trying to find a relationship between the masses of reacting substances by keeping it a simple whole number ratio.

Sometimes students may get the ratio as 1:9 by rounding off 11% as 10% and 89% as 90%. This is a less precise ratio than 1:8, because rounding off 11% to 10% leads to a 10% error in the value of one of the divisions. In direct division, such error is not involved.

Playing with the results...

Q2. People have always tried to write shortcut notations to represent information. If people wanted to write the information about the mass ratio of **A** and **B** in **X** as shorthand notation, how should they write it as?

Here students may write many different answers such as A_1B_8 , $1A-8B$, or AB_8 , or $A(1): B(8)$, or $(A, B) = (1, 8)$. There is no standard symbolic notation for this mass ratio in chemistry or physical sciences.

Q3. Usually gases could be mixed in any proportion. However, **X** had fixed proportion of masses of **A** and **B**. What did the fixed mass ratio tell about **X**?

Here, students may say different things like **X** always has same properties, or **X** may have some fixed structure in it.

Many philosophers since ancient history said that all matter consists of very small unit particles (called atoms). However, no one had seen or measured the mass of these unit particles. Now even if they assumed that **A**, **B** and **X** consisted of unit particles, it was unknown how these unit particles combined to give a fixed mass ratio at bulk scale, every time.

If these substances consisted of unit particles, then there were two possibilities:

- (i) different particles of a given substance had same mass.
- (ii) different particles of a given substance had different masses.

Q4. If different particles of **A** had different masses, just like different particles of sand are different, would the number of particles in any 100 g sample of **A** be always the same or different? Explain.

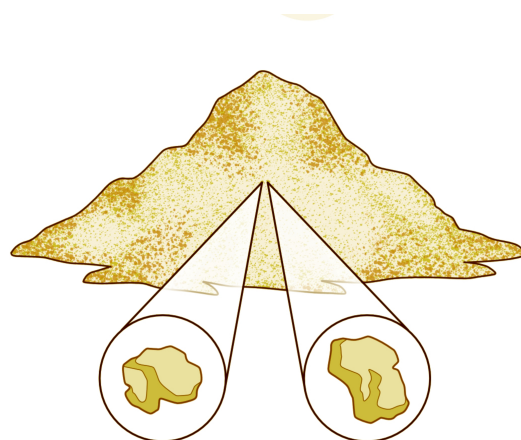


Figure 3: In a heap of sand, each particle of sand is different from all other particles.

If all particles of **A** had exactly the same mass, the number of particles in any sample of 100 g of **A** would be always the same. But if the particles had different masses, then the number of particles in two 100 g samples may be same or may not be the same.

Q5. In which of the above two possibilities, (i) or (ii), the mass ratio of **A** and **B** in **X** would always be the same? Explain.

Q6. What other condition about the particle combinations in **X** is necessary to explain the constant mass ratio of **A** and **B** in **X**?

If all particles of **A** are of same mass, and all particles of **B** are of same mass, then the mass ratio of **A** and **B** in **X** would always be the same. If the particle masses of a substance vary, then in some samples, mass ratio may be approximately same, but it will not always be the same. Another condition is that the ratio of number of particles of **A** and **B** in every particle of **X** should always be the same.

It should be noted that assuming particles of a substance to be identical was a big leap of imagination and contradictory to common experience, because in nature no two particles of any substance are identical. Like a heap of potatoes will always have potatoes of different masses, and two particles of sand or soil are never identical.

Back to the past...

Around 1800, a pharmacist in France, Mr. Joseph Louis Proust proposed that a fixed composition of elements by mass is a characteristic property for some substances which we can call compounds. These "compounds" were different from mixtures, which could have varying composition. Since many substances were known by then that had fixed composition, this hypothesis of Mr. Proust came to be known as the law of constant proportion for compounds.

Playing with the results...

If all particles in an element have same mass, then total masses of **A** and **B** in a certain amount of **X** can be written as:

$$\text{Mass of A in X} = \text{mass of 1 particle of A} \times \text{number of A particles in X}$$

$$\text{Mass of B in X} = \text{mass of 1 particle of B} \times \text{number of B particles in X}$$

The mass ratio of **A** and **B** in **X** was obtained from experiments. Therefore, if one knew the ratio of particle masses of **A** and **B**, then the ratio of number of **A** and **B** particles could be obtained, and vice versa.

Two students, Kamal and Amina were reading this history and were trying to find possible ratio of number of particles of **A** and **B** in **X**.

Q7. Amina wanted to take the simplest possibility that the particle mass of **A** is same as that of a **B** particle. For Amina's assumption, find the ratio of number of particles of **A** to **B** in **X**.

(1:8)

Q8. Amina chose shorthand symbol of **X** as A_yB_z , where y and z are number of particles of **A** and **B** in a particle of **X**, respectively. Then what would Amina write the symbol of **X** as?

(A_1B_8)

Q9. Kamal assumed that the mass of an **A** particle is 4 times the mass of a **B** particle. For Kamal's assumption, what would be the symbol of **X**?

(A₁B₃₂)

Back to the past...

Now let us go back in 18th century and see what assumptions the scientists made about **X**.

In 1787, a 21 year old professor of mathematics and natural philosophy in England, Mr. John Dalton, had an unusual interest in the nature of the atmosphere. He continued his study on atmospheric gases even after losing his job in 1789. He proposed that all substances are made of particles. He also made a very unusual and bold assumption giving a face to the modern atomic theory:

- all particles of the same substance must be having the same mass and be identical in other properties as well
- particles of different substances must have different masses

In 1804, Mr. Dalton published a book "*A New System of Chemical Philosophy*". In this book, he wrote that, the ratio of the number of particles of elements in a compound can be expressed as a simple whole number ratio. For **X**, he made an assumption that the ratio of number of particles of **A** and **B** should be 1:1, and the symbol of **X** should be **AB**.

Q10. With Dalton's assumed symbol (**AB**) for **X** and assuming that the mass of a particle of **A** is 1 unit, what would be the mass of a particle of **B**?

Since mass ratio of **A** and **B** in **X** is 1:8, if mass of particle **A** is 1 unit, then mass of **B** particle is 8 units.

Thus, Dalton's simplifying assumption created a new way to understand compositions of substances. The experiments so far showed that there were substances which always had same mass ratio of constituents (elements) and these substances were called compounds. Also, as per Dalton's theory, all elements should contain identical particles. However these developments were still insufficient to arrive at fixed chemical symbols of compounds. Some other information was also required. For **X**, this information came from volume measurements of reacting gases and their gaseous products, and some more theoretical assumptions, which are described in the next task.

Task 3: The Mystery of Volume Ratios: The Concept of Molecules

At the end of 18th century in England, Mr. Cavendish and Mr. Priestly found a relationship between volumes of reacting gases combining to produce **X**. This finding was later confirmed in 1808 by a French Chemist Mr. Joseph Gay-Lussac. They had found that to form **X**, the volume of gas **A** used was always 2 times than that of gas **B** used, at the same temperature and pressure. Also, **X** could be liquid or gas, depending on the temperature and pressure. When 2 L of **A** combined with 1 L of **B** at high temperatures, 2 L of gaseous **X** was obtained at the same (high) temperature.

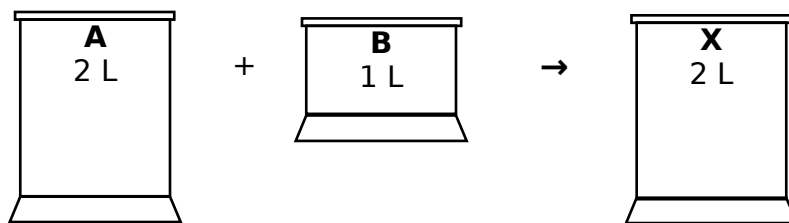


Figure 5: Reacting gases of specific volumes

Mr. Anthony Carlisle and Mr. William Nicholson had also found the volume ratio of **A** and **B** gases obtained from electrolysis of liquid **X** to be about 2:1.

These volume ratios were puzzling for multiple reasons. Why should the volume of reacting gases be fixed? These ratios indicated that:

I. the number of particles **per unit volume** in any samples of gas **A** at given pressure and temperature is always the same! [or the average volume of each gas particle is always the same]

II. the number of particles of **A** and **B** combining together to produce **X** were also fixed?

These inferences can be justified based on an argument similar to that for mass ratio. The volume ratio **A** and **B** obtained from **X** would be constant ALWAYS only if the average volume occupied by the particles of **A** is same and similarly with particles of **B**. If particles of **A** can have different spacious extent, then volume of **A** obtained from constant volume of **X** would vary at different times.

In terms of idea, however, this is more complex because it involves the question of whether particles are stacked on the top of each other or have spaces in between. If we imagine that the particles are stacked on each other, then it is enough to imagine that the size of the particles of a substance is always the same. But if we imagine the particles have spaces in between, then we also need to imagine that the average space in which particles move around at a given temperature and pressure is also constant. Imagining this is difficult if we assume random distribution of particles in space.

III. mass percentage of **B** used for **X** was higher and volume was lower than that of **A**!

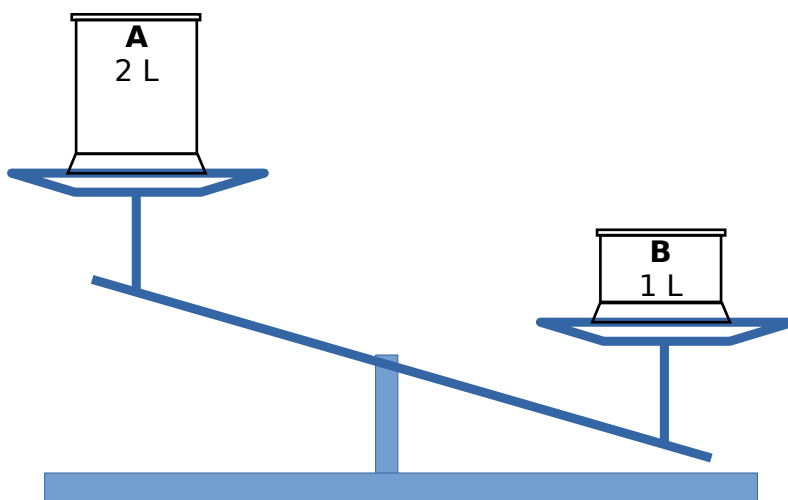


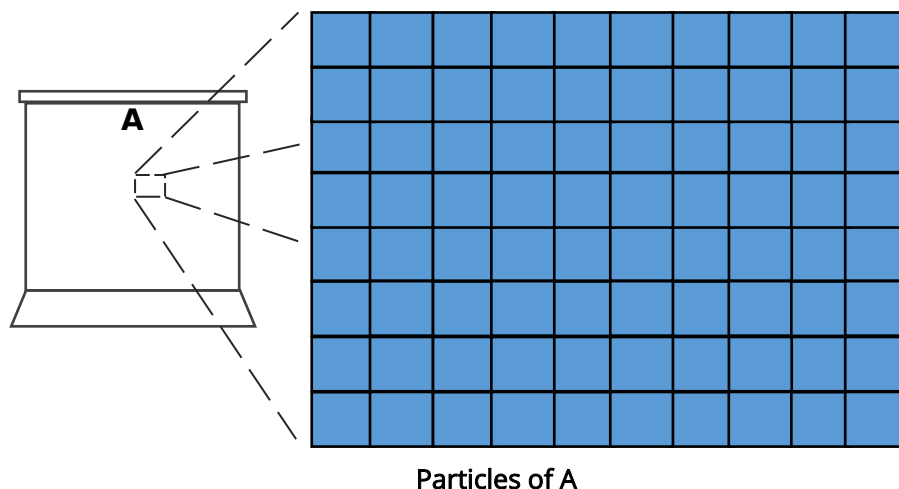
Figure 6: Mass and volume comparison of A and B

At that time, it was unknown how particles were arranged in space. Two possibilities could be thought about spatial arrangements:

Model I: the particles are stacked over each other and are roughly stationary with negligible spaces between them (similar to solids). John Dalton proposed that these stacked particles could expand and shrink. This expansion and contraction could allow gasses to flow easily, and expand and contract on heating and cooling.

Model II: the particles are small and have spaces between them, and keep moving in this space. In this model, all particles could eventually fall down under gravity, and gases could not be stable. Thus no one could explain how the gases could be stable with particles having spaces in between. [It took another 100 years to understand how moving particles in gases, with lots of empty space between them, could be stable.]

Hence, the common imagination was that the particles were stationary and stacked over each other. Since no one had ever seen the shape of particles in gases, Mr. Dalton imagined particle shapes to be cubical (the size of which could change with heat). Though today we know Model I to be incorrect, but historically following this model can help us in gaining interesting insights. Consider the following diagram showing cubical particles arranged in **A**.



Particles of A

For reference, atoms with cubical boundaries as imagined by John Dalton are shown in this figure.

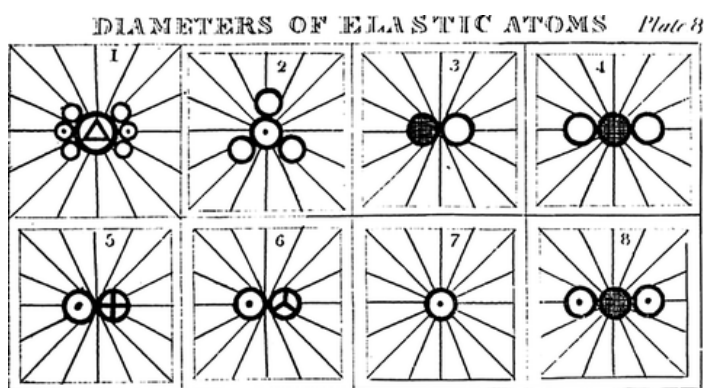


Figure T1: Atoms of different substances with cubical envelopes originally drawn by John Dalton in his book "A New System of Chemical Philosophy"

Playing with the results...

Since average volume of particles in a gas was always same at a given temperature (irrespective of Model), the following 9 cases can be thought of for the experimental mass and volume ratios of gases **A** and **B**:

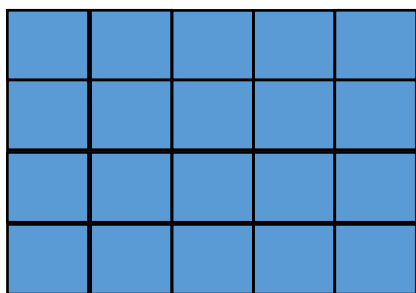
Case no.	Mass of particles of A and B	Average volume of particles of A and B
I	Same	Same
II	Same	B is bigger
III	Same	A is bigger
IV	A is Heavier	Same
V	A is Heavier	B is bigger
VI	A is Heavier	A is bigger
VII	B is Heavier	Same
VIII	B is Heavier	B is bigger
IX	B is Heavier	A is bigger

Q1. Four of the above cases are not possible based on the experimental results about the mass and volume ratios of **A** and **B** in **X**. Identify those four cases.

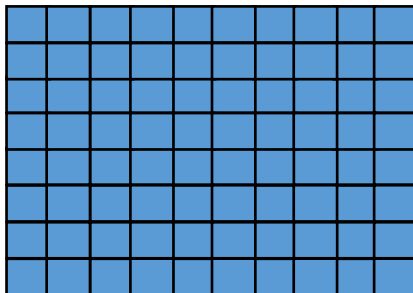
The following cases are not possible:

Case no.	Mass of particles of A and B	Average volume of particles of A and B
I	Same	Same
II	Same	B is bigger than A
IV	A is Heavier	Same
V	A is Heavier	B is bigger than A

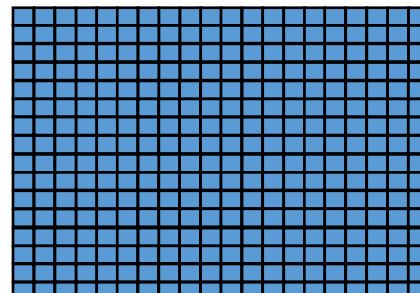
Q2. For **B**, three different possibilities are shown in P1, P2 & P3. The **A** particles are the same size as P2. For the remaining 5 cases, write in the table below, how the particle arrangements in **B** might look like in comparison to **A**.



P1



P2



P3

Case no.	Particles in A	Particles in B (P1 or P2 or P3)
	P2	
	P2	
	P2	
	P2	
	P2	

Case no.	Particles in A	Particles in B
III	P2	P3
VI	P2	P3
VII	P2	P2
VIII	P2	P1
IX	P2	P3

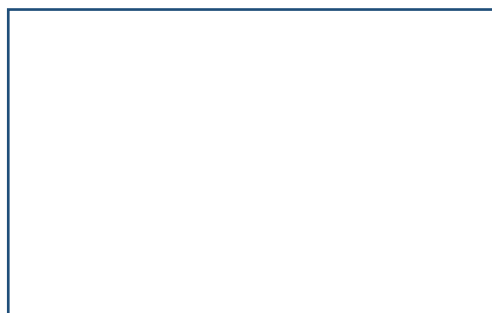
Q3. As per the given experimental results, which of the above cases are likely to be more correct and why?

Based on data provided here, all remaining 5 cases are likely to be possible. There was no evidence if particles of **B** are heavier, lighter, bigger or smaller than that of **A**. It is important to realize here that without any strong reason or evidence, none of the possibilities can be ruled out.

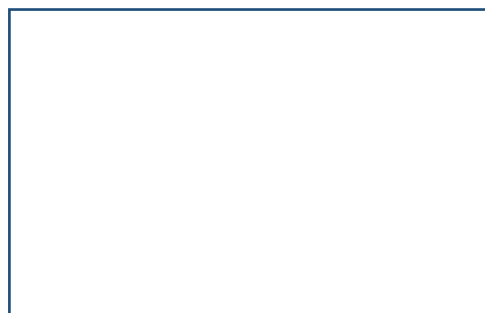
The most important purpose of this question is to help students realize that the data about volume ratio prompted a problem about stacking of particles, particularly for gases. Mr. Dalton also could not think of empty spaces between particles and he saw gases consisting of particles stacked together.

The real problem in this picture was in explaining diffusion of one gases into other gases, which requires particles to move in between other particles. Mr. Dalton explained diffusion of two dissimilar gases by saying that particles of different sizes (of the two gases) stacked on one another would keep on tumbling and hence keep on mixing.

Q4. If we imagine bigger particles to be heavier, then for one of the cases, none of the above diagrams can explain the particle arrangements in **A** and **B**. Which case it is? Draw the particle arrangements for **A** and **B** in the space below that can explain this case.



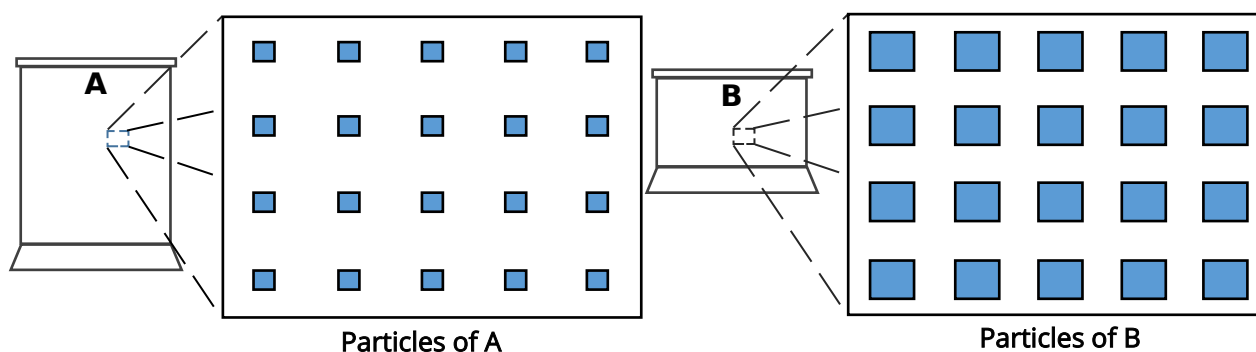
Particles of A



Particles of B

Here students can draw any other possibilities that comes to their mind. It can be different shapes of the particles, whether they are ordered or random, have space within or not, etc. Pedagogically, it can help see alternate conceptions in the mind of students.

Particles of **B** are heavier as well as bigger than particles of **A**. In such case, there must be empty spaces between neighboring particles (of at least **A**).



Particles of A

Particles of B

Back to the past...

Unfortunately, the data presented so far was insufficient to establish the chemical symbol for **X**. No one could count the number of particles in a given mass or volume of a gas. Based on patterns in his experimental results, Mr. Gay-Lussac assumed that equal volumes of different gases should be containing equal number of particles.

Q5. If equal volumes of two gases have same number of particles, then which of the above cases can be rejected?

All the cases where the average volumes of particles of **A** and **B** are not same (i.e cases II,III,V,VI,VIII, and IX) can be rejected.

Q6. With the assumption that equal volumes of different gases have equal number of particles, 2 L of **A** should contain twice the number of particles as in 1 L of **B**. If two particles of **A** combine with one particle of **B** to give one particle of **X**, then how many litres of gaseous **X** would be obtained with 2 L of **A** and 1 L of **B**? Explain.

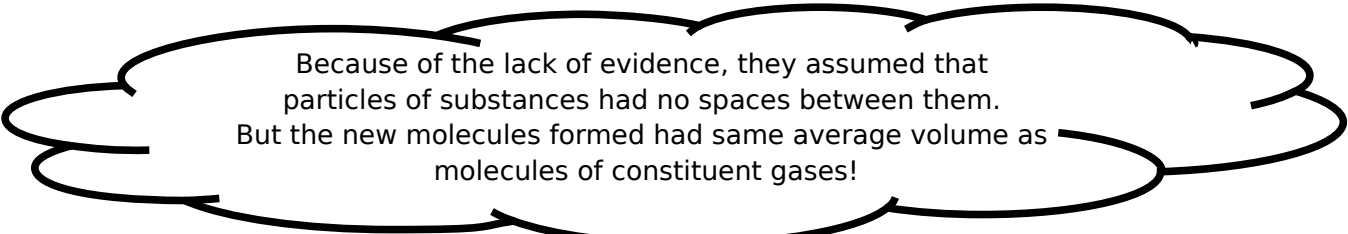
The number of particles of **X** formed would be same as the number of particles of **B**, thus 1 L of **X** should be obtained.

Mr. Dalton did not accept Mr. Gay-Lussac's reasoning because if 1 L of **A** had same number of particles as 1 L of **B**, and if two particles of **A** combine with one particle of **B** then 2 L of gaseous **X** could not be obtained. He argued that if particles of different elements had different masses, then their sizes should also be different and they should have different per particle volumes.

Q7. If particles of different elements have different average volumes, then which of the above cases can be rejected?

Cases I, IV and VII have to be wrong because they pertain to particles of both A and B to be of the same size (i.e the average volume).

In 1811, an Italian physics professor Mr. Amadeo Avogadro published a solution to the volume problem. He wrote that if the smallest particles of elements could break into two half particles, then two particles of **A** (i.e 4 half particles of A) would combine with one particle of **B** (i.e 2 half particles of B) to give two particles of **X**. Thus, Mr. Avogadro brought the idea of molecules and that molecules can break into two smaller particles (which now everyone knows as atoms). In other words, what was being considered as (fundamental) particles so far, were actually molecules. Molecules could break further to give atoms.



Because of the lack of evidence, they assumed that particles of substances had no spaces between them. But the new molecules formed had same average volume as molecules of constituent gases!

In addition, Mr. Avogadro also supported Mr. Gay Lussac's reasoning and showed the necessity to assume that "equal volumes of all gases at the same pressure and temperature contain equal number of particles" (Case VII) to explain the above experimental observations.

In our current molecular understanding of gases, the average volume occupied by particles of all (ideal) gases is same at the same temperature, whether molecules contain one atom, two atoms or 8 atoms. This approximation holds valid for most gases because actual space occupied by the molecules is negligible (about one thousandth) compared to average volume of space per molecule of gas. This average volume is defined by the average speed of the molecules of gases, and remains constant because average distance between neighboring molecules in a gas, in all three dimensions, remains constant at a given temperature.

Q8. If we accept Avogadro's hypothesis about half-particles (atoms), then what must be the ratio of number of half-particles of **A** and **B** in **X**. Thus, what should be the chemical symbol of **X**?

Ratio of number of half-particles of **A**: **B** = 2:1, chemical symbol: **A₂B**

Task 4: The Major Learnings

Q1. If the formula of **X** is as per Avogadro's hypothesis and mass of an atom of **A** is taken to be 1 unit, then what must be the mass of an atom of **B**.

2 atoms of **A** have mass of 2 units.

Mass of **B** in **X** is 8 times that of **A**. Thus mass of atom of **B** is $8 \times 2 = 16$ unit

Q2. How many years did it take after the first laboratory synthesis of **X** to arrive at its modern chemical symbol (molecular formula)?

About 30 years.

Q3. Can you now guess what is compound **X**?

X is water, **A** is hydrogen and **B** is oxygen. This, students can possibly predict, from currently known atomic masses of elements.

Q4. List the three experimental results and four major assumptions that were necessary to arrive at the modern chemical formula of **X**.

Experimental results:

a) **X** consists of two different substances **A** and **B** (gases), hence it is not an element.

b) Ratio of masses of **A** and **B** in **X** is always 1:8.

c) 2 L of gaseous **A** combines with 1 L of gaseous **B** to give 2 L of gaseous **X** at the same temperature and at atmospheric pressure.

Assumptions:

a) All substances (including liquids and gases) consist of particles.

b) Particles of an element are exactly alike in mass and other properties, and particles of different elements are different in mass and other properties.

c) Equal volumes of all gases consist of equal number of particles, at the same temperature and atmospheric pressure.

d) In many elements, the particles (molecules) can break into half particles (atoms) which can combine to give new particles (molecules) of another substances (called compounds).

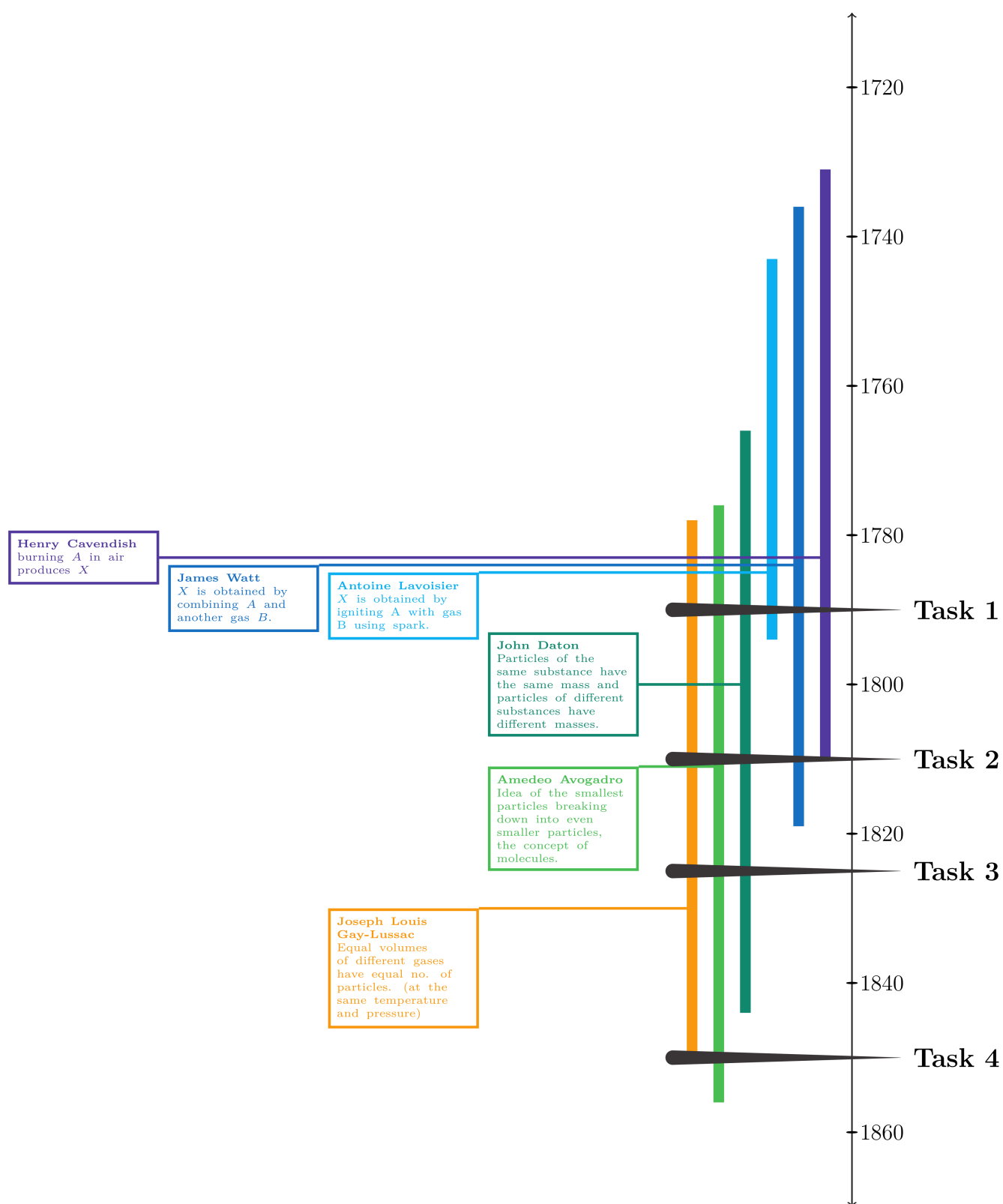


Figure 6: Timeline of – How “X” got its chemical description...

Suggested Readings:

- Aaron J. Idhe (1984), The development of Modern Chemistry, Dover Publications, Inc, New York. This book presents a very detailed history of various developments leading to modern chemistry.
- Anirban Hazra (2006), The Story of Chemistry, Vigyan Prasar. Available online at: <http://scipop.iucaa.in/Literature/storyofchemistry.pdf>. This book is a comic book written and illustrated for young children to make the story of chemistry interesting for them.
- Sushil Joshi, Uma Sudhir (2014), The story of Atomic Theory of matter, Eklavya, Bhopal. This book has detailed description of experiments and ideas that went into development of atomic theory with some interesting illustrations and suggested experiments.

References:

- a) Henry Cavendish's 1784 paper: <http://rstl.royalsocietypublishing.org/content/74/119>.
- b) James Watt's 1784 paper: <http://rstl.royalsocietypublishing.org/content/74/329>.
- c) Antoine Lavoisier' 1783 report: Observations sur la Physique, 23, 452-455 (1783).
- d) Pictures were sourced from
http://www.pci.tu-bs.de/aggericke/Personen/Gaylussac_Biography.html,
www.worldatlas.com/webimage/countrys/eu.htm,
fr.wikipedia.org/wiki/Fichier:Antoine_Laurent_de_Lavoisier.png