

## How "X" got its chemical identity

### 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<sub>2</sub>O, lime as CaO, cane sugar as C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>. For many substances, the origin of these alphabets and numbers has a long history.

In this Learning Unit, we will look at how the numbers in the molecular formula of one such substance came from. This became possible only after technologies were 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 two centuries ago.

II. 'Playing with the results': In these sections, you will explore different ways of interpreting and representing 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. Pierre-Joseph 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. (refer Figure 1) Let us call this burning gas A. Mr. John Warltire in England also observed the same phenomena. Four years later, an English priest, Dr. Joseph 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. Henry Cavendish (a physicist in England), Mr. James Watt (an engineer in Scotland), and Mr. Antoine Lavoisier (a tax collector and a chemist in France).

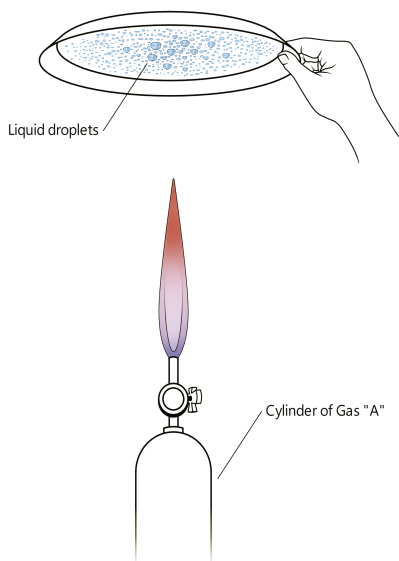


Figure 1: Mr. Macquer's experiment

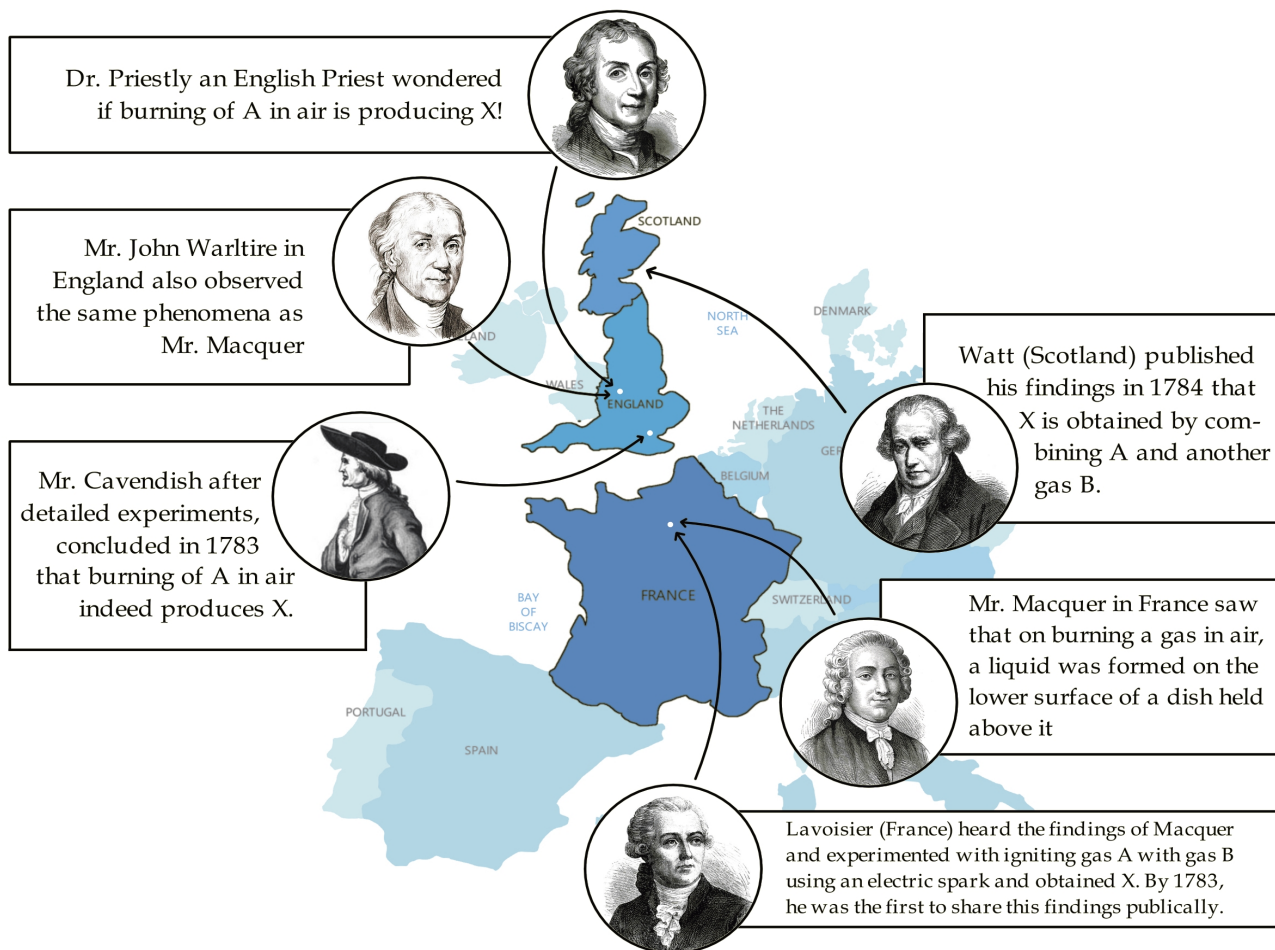


Figure 2: Experiments done by various people across Europe

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

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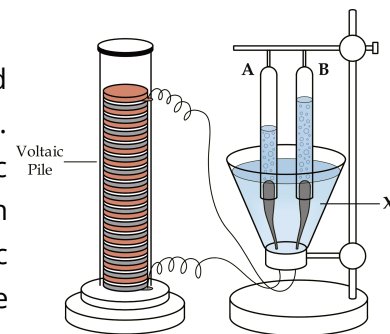
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Mr. Lavoisier also measured the mass of **X** formed and found it to be same as the sum of masses of **A** and **B** used.

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 with wet tissues in between. 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 did not?

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### 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)

## 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.

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### 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?

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**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 us about **X**?

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### Back to the past...

Since ancient history, many philosophers 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. So 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.

### Playing with the results...

**Q4.** In a handful of sand, all particles seem to be of the same size. But if we observe closely, each particle is different in shape and size. If different particles of **A** had different masses (like sand) would the number of particles in any 100 g sample of **A** be always the same or different? Explain.

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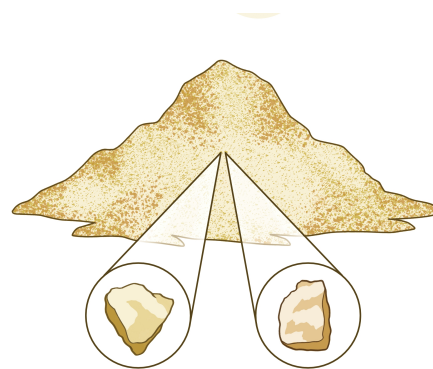
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**Figure 3:** In a heap of sand, each particle of sand is different from all other particles.

**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.

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

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### 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 the 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**.

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**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 shorthand symbol of **X** as?

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**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 shorthand symbol of **X**?

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### Back to the past...

Now let us go back in 18<sup>th</sup> 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 titled "*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**?

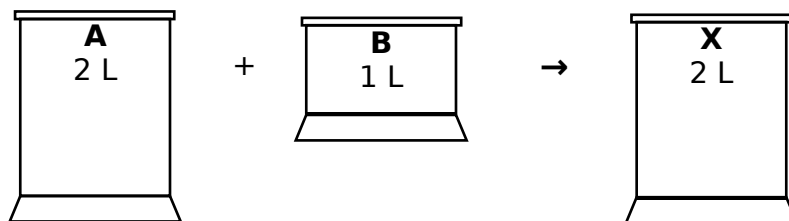
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Thus, Dalton's simplifying assumption created a new way to understand compositions of substances. The experiments so far showed that there were substances which always had same mass ratio of constituents (elements) and these substances were called compounds. Also, as per Dalton's theory, all elements should contain identical particles. However these developments were still insufficient to arrive at fixed chemical formula 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 18<sup>th</sup> 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. In 1800s, 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.

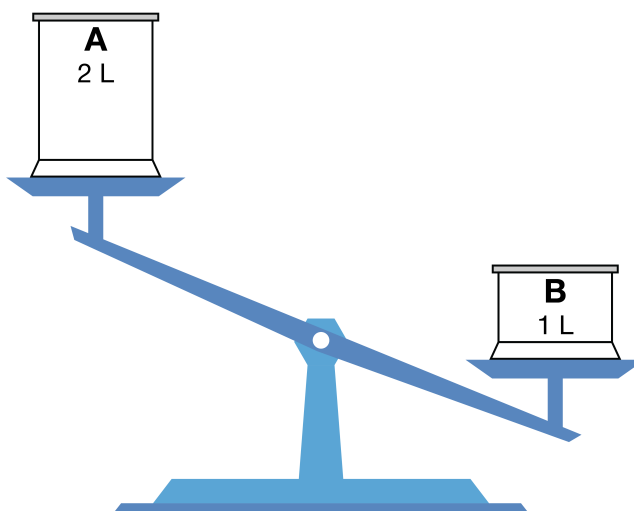
Also, X could be liquid or gas, depending on the temperature and pressure. When 2 L of A combined with 1 L of B at high temperatures, 2 L of gaseous X was obtained at the same (high) temperature.



*Figure 5: Reacting gases of specific volumes*

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

- I. at a given temperature and pressure: the number of particles **per unit volume** of gas A is always the same; which also implies that the average volume of each particle of A is always the same. The same is also true for gas B.
- II. the number of particles of A and B combining together to produce X were also fixed?
- III. mass 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*

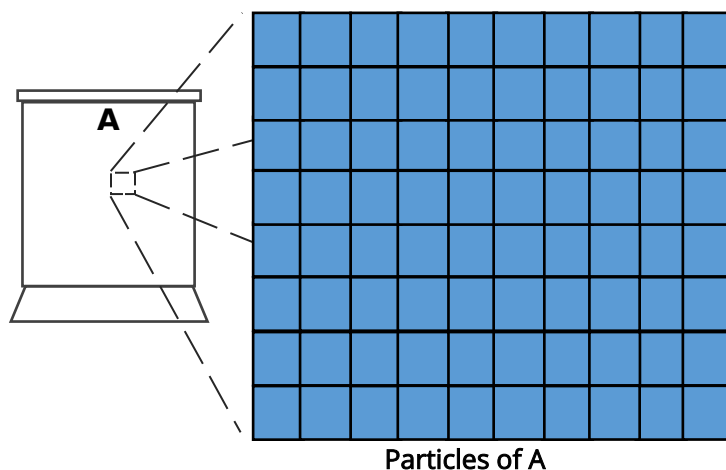
At that time, it was unknown how particles were arranged in space. Looking at the ideas on this which have been discussed historically, we observe two models of arrangement of particles which were discussed at different times:

**Model I (a Static model):** The particles, even in gases, are stacked over each other and are roughly stationary with negligible spaces between them (as in solids). John Dalton proposed that these stacked particles could expand and shrink. This expansion and shrinking could allow gases to flow easily, and expand and contract on heating and cooling, respectively.

**Model II (a Dynamic model):** 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, then what keeps the gases stable. No one could explain how the gases could be stable with particles having spaces in between. [It took

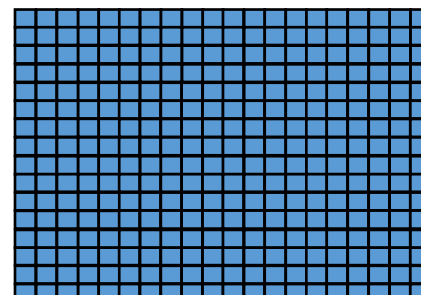
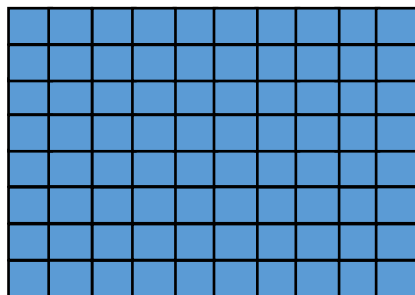
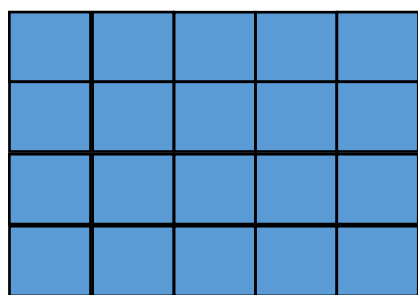
another 100 years to understand how moving particles in gases, with lots of empty space between them, could be stable.]

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 shapes of particles to be cubical (the size of which could change by 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 gas **A**.



### Playing with the results...

Particles of 3 different volumes are shown in P1, P2 & P3. Suppose the **A** particles are of volume as in P2. Particles of **B** can be of the same volume, larger (as in P1) or smaller (as in P3).



P1

P2

P3

If volume of each particle in a gas was always same at a given temperature (irrespective of Model), then 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 <b>A</b> and <b>B</b>	Volume of particles of <b>A</b> and <b>B</b>
I	Same	Same
II	Same	<b>B</b> is bigger
III	Same	<b>A</b> 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

Consider Case II. If particle mass of **A** and **B** is the same, then **B**, which is more in mass than **A** (in **X**), would have more particles than **A** (from the mass ratio you calculated in Task 2, you can also know how many times more particles of **B** are there than that of **A**). Further, **B** which has more and bigger particles cannot occupy lower (half) volume than **A**. Thus, this case is not possible.

**Q1.** Similarly, based on the experimental results about the mass and volume ratios of **A** and **B** in **X**, 3 more cases are not possible. Identify those three cases.

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For the remaining 5 cases, write in the table below, what would be the particle size of **B** in comparison to **A**.

Case no.	Particles in <b>A</b>	Particles in <b>B</b> (P1 or P2 or P3)
	P2	
	P2	
	P2	
	P2	
	P2	

**Q3.** As per the given experimental results, which of the above cases you think is most likely correct and why?

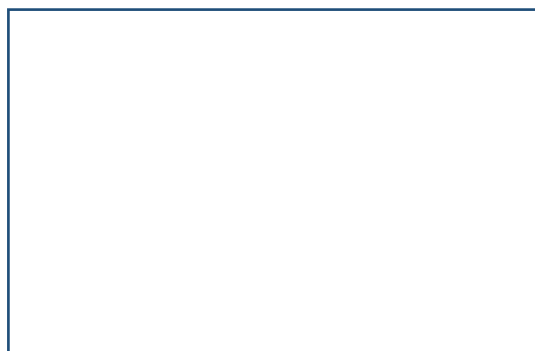
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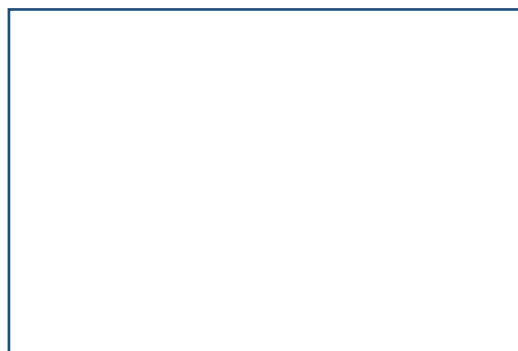
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**Q4.** If we imagine bigger particles to be heavier, then for case VIII, none of the above diagrams (P1, P2, P3) can explain the particle arrangements in **A** and **B**. Draw the particle arrangements for **A** and **B** in the space below that can explain this case.





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. Experimental volume ratios of combining gases by Mr. Gay-Lussac and others indicated that equal volumes of different gases should be containing equal number of particles. (This was later theoretically proposed by Swedish chemist Berzelius.)

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

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**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.

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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?

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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 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.

**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**?

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#### 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**?

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

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

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

Experimental results:

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Assumptions:

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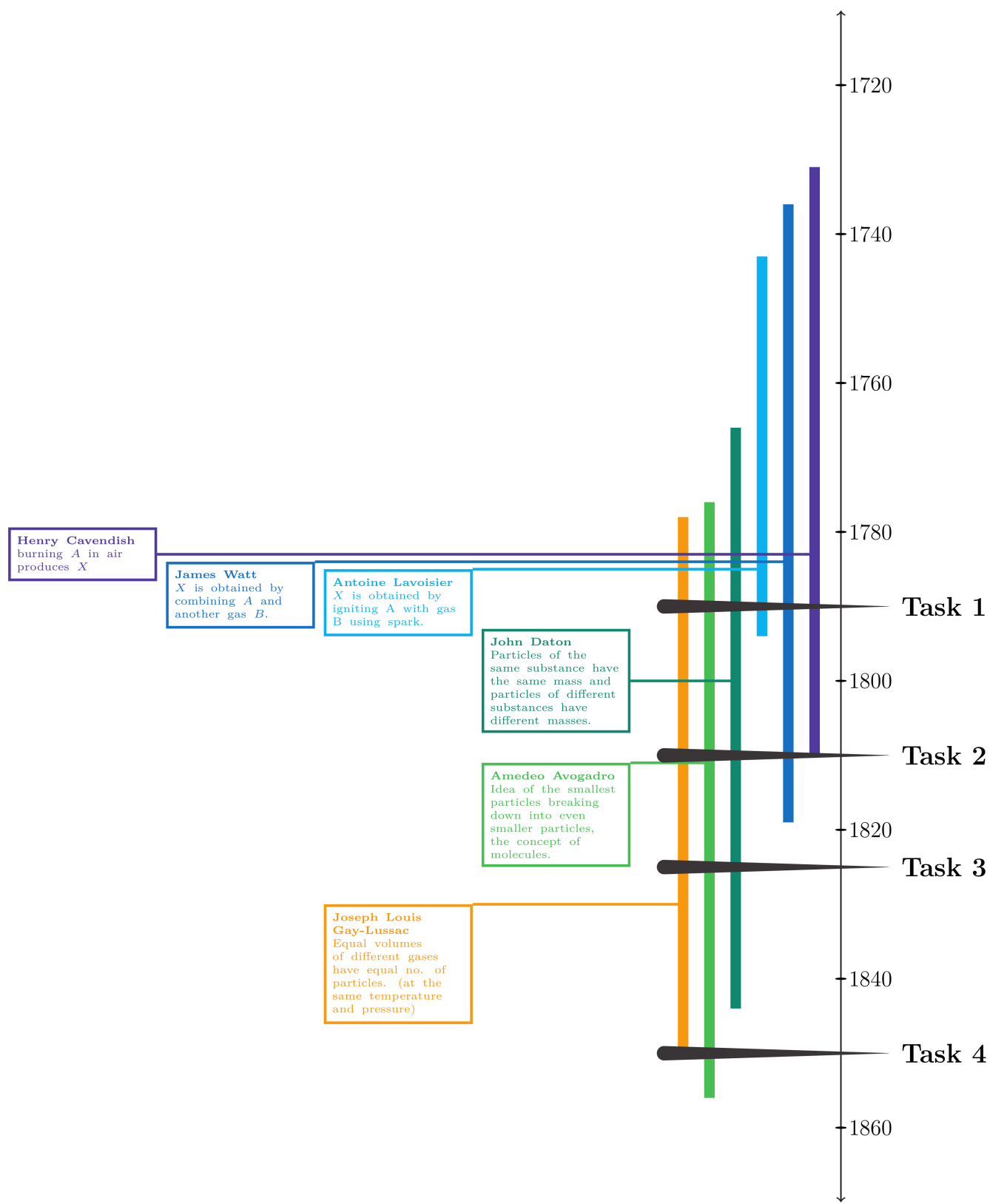


Figure 6: Timeline of – How “X” got its chemical description...

**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](http://www.pci.tu-bs.de/aggericke/Personen/Gaylussac_Biography.html),  
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