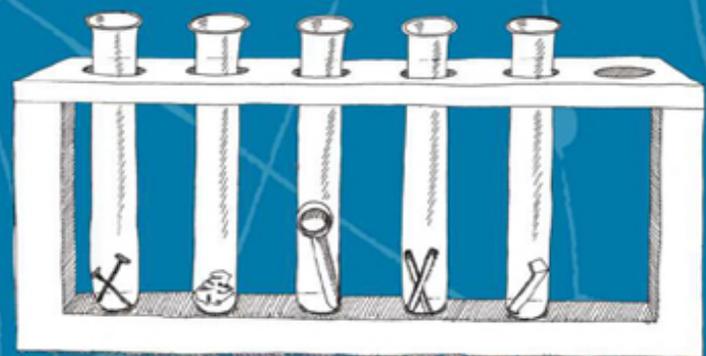
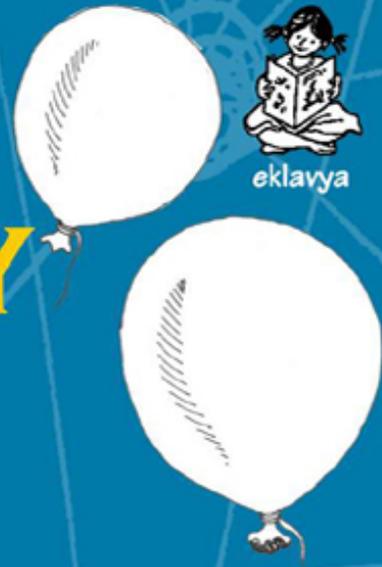


# THE STORY OF ATOMIC THEORY OF MATTER



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an eklavya publication

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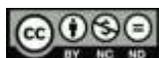
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March 2017/2000 copies

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Paper: 80 gsm and 300 gsm paper board

ISBN: 978-93-81337-74-5

Price: ₹ 135.00

This edition has been developed with support from Parag Initiative of Tata Trusts.

Published by: Eklavya  
E-10, Shankar Nagar BDA Colony  
Shivaji Nagar, Bhopal - 462 016 (MP)  
Phone: +91 755 255 0976, 267 1017  
[www.eklavya.in/books@eklavya.in](http://www.eklavya.in/books@eklavya.in)

Printer: RK Secuprints Pvt. Ltd, Bhopal (MP) +91 755 268 7589

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## WHY WAS THIS MODULE DEVELOPED?

This module is part of a series being developed by a high school science group coordinated by Eklavya, an organisation based in Madhya Pradesh that conducts research in education and prepares curricula and related material for school education and teacher orientation. The high school science group is a loose agglomeration of scientists, educationists, college and school faculty, social activists and others who are concerned about the status of science education in Indian schools and would like to introduce contemporary ideas and approaches in science pedagogy into the curriculum.

Their work draws inspiration from the Hoshangabad Science Teaching Programme (HSTP), an innovative science education programme that was conducted for 30 years from 1972 to 2002 in around 800 government and private middle and higher secondary schools across 14 districts of Madhya Pradesh, reaching out to around 50,000 students annually.

The HSTP sought to improve science teaching in middle schools (classes 6 to 8) by incorporating ideas and approaches in science pedagogy that were influencing school science teaching across the world in the 1960s and 1970s. Its basic premise was that rote learning is antithetical to science teaching and students aged 11 to 14 years should learn science by actually doing experiments in the classroom and interacting with their immediate environment to 'discover' scientific laws through a process of observation, analysis, reasoning and discussion.

The HSTP's emphasis on the 'scientific method' saw learning largely structured around experiments, with many concepts thought to be too abstract for the middle school age group being deliberately excluded. The curriculum developed for this school stage, while broadly adhering to the state curriculum framework, focused on concepts and ideas that were considered crucial to developing an understanding of science, and fostered skills to encourage the self-learning abilities of students.

However, field experience saw the programme's almost exclusive focus on experiment and the 'discovery' approach being tempered in the later stages to incorporate more theoretical explanations and descriptive details as well as stories about the historical development of ideas and concepts in science, among other things.

The high school science group takes a similar age-related approach to science teaching at the high school level (classes 9 and 10), introducing more theoretical content, investigative activities and science history in keeping with the growing comprehension abilities of the students, but still retaining an 'experiment' core and excluding concepts that can be better treated at the college and university level.

The series of science modules being developed for this stage of schooling broadly covers the syllabus prescribed by the various examination boards at the national and state levels. These modules are addressed to both students and teachers and contain additional resource materials that teachers would find useful in classroom instruction.

## WHAT IS THE STRUCTURE OF THE MODULE?

This module discusses the subject of 'matter', a concept that is yet to be definitively defined in science. It is primarily meant as background reading for teachers to strengthen their understanding of the concepts discussed.

Matter is everything you see around you – trees, birds, air, stones, buildings, cars... your friends. It's the stuff things are made of and is generally defined as anything that has mass and volume (which is the space it occupies).

Matter is composed of atoms, and atomic theory is central to chemistry. Natural systems are fundamentally chemical systems.

Atoms (which combine to form molecules) constitute the elements we see in nature. Each element consists of identical atoms and elements can be distinguished from one another because their atomic weights differ. Atoms of different elements combine in chemical reactions to form compounds. The atoms and molecules of the elements/compounds that take part in reactions form new combinations that constitute the products of the reaction.

These processes are governed by specific laws. It took over 2,000 years for humankind to develop an understanding of atomic theory and the laws that underlie the way nature works.

It is this crystallised knowledge that students are expected to understand and internalise in their five years of study at the middle and high school level. But, given our long experience of working with school-children, we have been selective in choosing the content of this module, our judgment governed by what we feel students of this age-group can understand, internalise and fruitfully relate to.

The module is divided into three parts.

The first part presents a historical overview of how our understanding of atomic theory and the nature of matter evolved. In essence, it is also a history of the birth and development of the science of chemistry. Modern-day chemistry can trace its ancestry to the quasi-spiritual attempts of alchemists to change base metals into gold but subsequently gained a solid 'scientific' foundation through investigative experiments conducted into the structure of matter. It is this structure that governs the chemical and physical properties and changes that are the basis of life. But one thing needs to be noted here. Although these investigations laid the foundation of chemistry as we know it today, they are largely multidisciplinary in nature, being profoundly influenced by progress in several fields of scientific study.

The second part lists some of the misconceptions students at the middle and high school level have about the particulate nature of matter. These misconceptions have been investigated and articulated through various studies conducted across the world among students of different age groups, beginning with naïve conceptions of matter among young children based on the common sense that 'seeing is believing' and progressing to changing

perceptions, catalysed by classroom instruction, as the students move into the higher classes. The point of interest is the persistence of some of these naïve beliefs among students even after they gain insights into the particulate nature of matter with repeated instruction. It shows how difficult it is for them to take the step from 'seeing is believing' to an abstract concept about 'invisible' factors that may go against the grain of common sense.

That's why the approach we have taken in this module is influenced by an appreciation of these misconceptions. At the same time we have tried to point out what students need to know if they are to internalise the concept of the particulate nature of matter. We have also tried to identify some of the weak links in the way abstract concepts in atomic theory are treated in textbooks and in classroom instruction, which compound the comprehension problems of students.

The third section is a set of experiments that introduces students to facets of chemistry that are crucial for gaining an understanding of atomic theory. In a way they seek to prepare the ground for a better understanding of the basic premises of the science of chemistry – its foundation and framework. Hopefully, these experiments will provide students with the minimum necessary 'chemical experiences' they need to appreciate why the particulate model of matter provides the most logical explanation of change in various phenomena, which are basically chemical in nature. So it would be best if students perform these experiments before embarking on a study of this module.

And a final word. The module discusses the atom from the point of view of understanding chemical phenomena. But there is more to the atom, such as its internal structure of a nucleus with protons and neutrons and orbiting electrons. There is the atomic structure at the quantum level. There is also the motion of atoms, both intrinsic and extrinsic. All this is not dealt with here in this module. Some aspects of the motion of particles finds place in another module 'Heat and Temperature', developed as part of this series. But what should be noted is their relevance to getting a better understanding of during the chemical change and behaviour of matter. It goes to show the highly interdisciplinary nature of science where the distinction between subjects tends to blur. If we go into the subject of organic molecules and the chemistry of life, the overlap of chemistry, physics and biology becomes even more evident.

The basic idea of the module is to help the students progress from their common-sense conceptions about matter through instruction to a better appreciation of the particulate nature of matter, which is the basis of chemistry. The importance of appreciating the particulate concept of matter is best summed up in the words of the late Nobel laureate physicist Richard Feynman:

*If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis 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.*

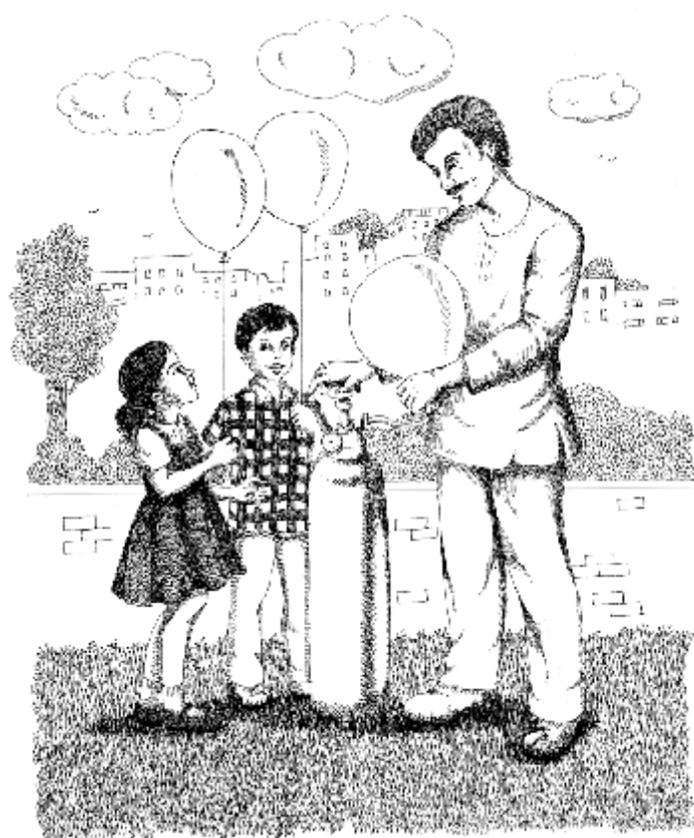
## PART 1

### A HISTORICAL PERSPECTIVE OF HOW OUR UNDERSTANDING GREW

We see many things around us, each different from the other. We also see many changes happening in our daily lives. Water turns to ice in the freezer of a refrigerator. Ice cubes melt in a glass of lemonade and cool it. Wet clothes dry quickly if the sun is shining bright but take longer to dry on a rainy day. If we add a little lemon juice to milk, we get paneer. Sugar dissolves if stirred in a cup of tea.

Why is one thing different from another? Why does water freeze, and how does melting ice cool the lemonade? Where does the water go when wet clothes dry? Why do clothes take longer to dry on a rainy day? Where is the paneer hidden in milk and what separates it to leave behind the sour, watery whey? Where does the sugar in tea disappear?

There are many more such questions. How do we get a shiny metal like iron from a lump of reddish ore dug out of the soil? Why does this iron rust? Why do pipes corrode? Why does corrosion occur more rapidly in some seasons, and why is it a bigger problem in homes that are close to the sea? Why is it possible for gases to expand so much, and how is it that they can be compressed to such an extent? What happens to the air we breathe and the food we eat? Why do we grow older?



*How can so many balloons be filled from a small cylinder?*

All these are basically physical and chemical processes. They are linked to the atomic structure of matter. Atomic theory is considered central to understanding everything from heat (and temperature) to chemical reactions and stoichiometry. It is a model that helps us make sense of and make prediction about changes taking place around us.

## The Greeks

*Is the world permanent or in a state of constant flux? Is matter continuous or particulate? Aristotle's five elements battle it out with the atoms of Democritus.*

These kinds of questions about what makes the world tick have been raised by people from ancient times. Natural philosophers in most early civilisations – Chinese, Indian, Greek, Egyptian – wondered about the nature of matter and its structure but their thinking was mostly intuitive and speculative, with no experimental evidence. Nonetheless, they were keen observers of nature and deduced the causes of many natural phenomena through a process of logical reasoning. We have only very sketchy reports of this speculative thinking of the early philosophers, the best documented record being of ancient Greek civilisation. So this narrative begins with the Greeks and traces the influence of Greek thought in the development of modern science and chemistry.

One thing is clear. There were no uniform answers to these fundamental questions among the Greek philosophers, and several different points of view existed.

Thales of Miletus (625–545 BC) and his disciples believed everything in the world is made from one primary substance, viz. water, that is modified in various ways, while Anaximander (610–540 BC) said this basic material is characterless and limitless. There were others who thought differently from these 'monists', among them Empedocles (495–435 BC), who

believed there are four 'root' elements – earth, water, air and fire – that possess different properties and attract or repulse one another to varying degrees. So the variety we see around us is due to each substance possessing different amounts of each of these elements. For instance, a feather floats in air because it has more air in it and hence has the property of lightness. Or mud is a combination of water and earth, clouds are a combination of air and water, and lava a combination of earth and fire.



*Democritus reasoned that matter is made up of ultimate particles that he called atoms*

Aristotle (384-322 BC) added a fifth element, aether, which he said pervades the heavens and is unchangeable. We see similar strands of thought in other ancient civilisations such as India (prithvi, jal, agni, vayu, aakash) and China (metal, water, wood, fire, earth), with these basic elements and the different ways in which they combine even used to explain the moral characteristics and basic nature of people.

Plato (427-347 BC) took a different position, giving primacy to form (ideas) over matter. In his search for beauty and perfection he conceptualised matter in geometrical terms, saying the smallest units of which matter was composed were right-angled isosceles triangles. These triangles formed polyhedra that were the perfect solid shapes of the four elements in the early Greek concept of matter – tetrahedron (fire), octahedron (air), cube (earth) and icosahedron (water).

Another concern that engaged the philosophers of the time was whether the world is permanent and unchanging or in a state of constant flux. Heraclitus of Ephesus (535-475 BC) believed the world is constantly changing, that everything is in a state of flux (exemplified by his famous saying: “No man ever steps into the same river twice”). On the other hand, Parmenides of Elea (early 5th century BC) argued that everything is what it is and cannot become what it is not, so change is logically impossible.

Democritus (460-370 BC) suggested a possible way in which matter can change yet maintain its basic nature, building on the ideas of his mentor Leucippus (first half of 5th century BC). The master and the disciple suggested that all matter is composed of tiny units called atoms.

But what exactly is the nature of these particles? They gave the example of breaking a brick into two, then breaking the two halves and continuing the process over and over again. They concluded

that the process could not go on indefinitely because infinite division would create “cosmic



*Most of the books collected in an ancient library would have been written by Aristotle*

Johannes Kepler (1571-1630) and English physicist Isaac Newton (1642-1727). But his theory of matter continued to reign supreme until the 'birth' of modern science (see box: THE BIRTH OF MODERN SCIENCE AND THE SCIENTIFIC METHOD).

Fortunately, the Roman poet Lucretius (99-55 BC) preserved the concept of atomism, capturing it in one of his poems, "De rerum natura" (On the nature of things), a free prose translation of which is given below:

*Obviously it makes a great difference in these verses of mine in what context and order the letters are arranged. If they are not all alike, yet the most are so; but differences in their position marks the difference in what results [the words]. So it is when we turn to real things; when the combination, motion, order, position, shapes of matter [the atoms] change, so does the thing composed [out of these atoms].*

So the idea remained submerged for a long time till it was rediscovered in 1417. But it was only in the 19th century that Democritus' proto-atomic theory got a serious second look with the ideas propagated by the British chemist John Dalton (1766-1844).

## The birth of modern science and the scientific method

The 'birth' of modern science in the popular narrative is usually traced to the British scientist Francis Bacon (1561-1626), who wrote about a new method of scientific inquiry and logic in his *Novum Organum Scientiarum*, a philosophical work published in 1620.

Bacon rejected the Aristotelian approach to understanding nature, because the method was based on intuitive insights and speculation and could not be used to reproduce the natural phenomenon being investigated. He also rejected the method of the alchemists whose experimental investigations were rooted in myth, mysticism and religion. According to him, knowledge must come from a planned procedure based on sensory experience (empiricism), which included discovering evidence through experiments.

Bacon wrote that investigating a natural phenomenon is a process of breaking down the phenomenon into its constituent components (reductionism), analysing these components and then formulating general laws governing the phenomenon through a process of reasoning (inductive logic).

French philosopher Rene Descartes (1596-1650) also outlined the scientific method in his *Discours de la method*, published in 1637.

The use of the experimental method to investigate and test natural laws was perhaps best exemplified in the work of Galileo, who is credited with introducing another important aspect into our quest to understand nature – the use of mathematics.

This aspect, which he applied in the study of motion, is most clearly enunciated in his statement: "The book of the universe cannot be understood unless one first learns to comprehend the language and to read the alphabet in which it is composed. It is written in the language of mathematics, and its characters are triangles, circles, and other geometric figures, without which it is humanly impossible to understand a single word of it."

It is from here that the foundation of the scientific method as we know it today was laid. Science is a practical method of trying to understand natural phenomena and predict how they will progress. This method requires both experiment and theory to build explanations of what happens in the world. It can be conceptualised as a series of steps beginning with looking at nature (observing a phenomenon), asking a question about the phenomenon (formulating a hypothesis), performing an experiment to test the hypothesis, confirming or rejecting the hypothesis after analysing the experimental data, and finally subjecting the 'scientific law' distilled from the hypothesis to further experimental tests.

Basically, the approach is to let reality speak for itself, supporting a theory if its predictions are confirmed or challenging it when its predictions prove false. So it can be seen as a process of acquiring new knowledge or correcting/rejecting previous knowledge about the nature of the world we live in.

## The Alchemists

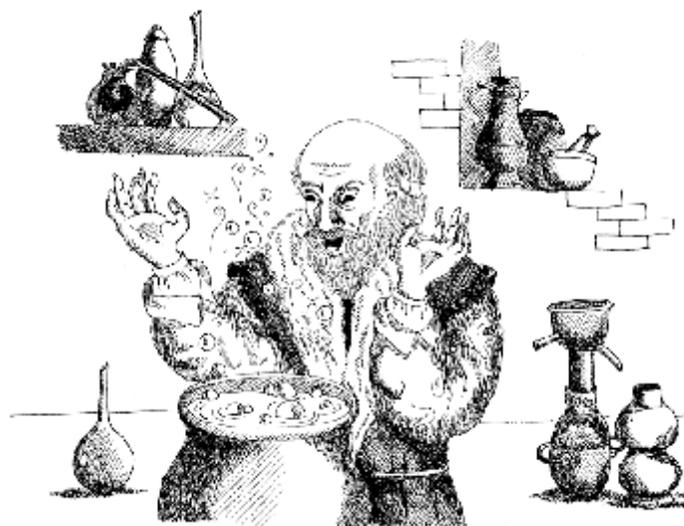
*Combining the 'yellowness' of sulphur and the 'shininess' of mercury to get gold... The journey from transmutation of substances to the birth of modern chemistry*

The overwhelming influence of speculative thinkers in the early history of science does not mean that there were no experimentally oriented developments taking place. There were many doers – practical-minded artisans and craftsmen who looked for solutions to everyday problems through a trial-and-error process. Such people were to be found in all civilisations across the globe from ancient times.

So we have weavers in India and elsewhere who learned the art of dyeing the clothes they wove in different colours with chemical dyes, many of them obtained from natural sources. Similarly, pottery, fermentation, metals and metallurgy, including smelting of copper and use of gold in jewellery, point to the use of chemical processes. Meanwhile ancient texts like the *Caraka Samhita* and *Susruta Samhita* (dating from the sixth to third century BC) point to animal, vegetable and earth products like minerals and metals being used for medicinal and therapeutic purposes.

The Chinese are reported to have discovered how to manufacture paper (105 AD) and gunpowder (11th century), while blacksmiths across the world learned the art of alloying metals to alter properties such as hardness and malleability. Among them were the early Gond tribals of Bastar region in India, who mastered the craft of smelting and bell metal alloying to

fashion artefacts and ornaments. Chemicals like phosphorus were isolated and many ancient systems of medicine, such as Ayurveda, learnt to extract or synthesise chemicals of medicinal value from natural sources.



*An alchemist surrounded by his apparatus*

There were also the alchemists flourishing in many civilisations across the globe who, more often than not, assigned mystical and spiritual causes to explain changes in the forms of substances they experimented with. They were influenced by Aristotelian ideas that everything is made up of combinations of five elements in different proportions that produce different qualities or characteristics. So a substance containing more of the elements of air and fire

would be light and shiny and if you could somehow remove the element air from the substance and substitute it with the element earth, you would get a new substance that was heavy and shiny.

This is exactly what the alchemists sought to do. They believed that one substance could be changed (transmuted) into another. They tried to extract the 'yellowness' of sulphur and the 'shininess' of mercury and combine them to get gold that is both yellow and shiny. This kind of reasoning also led them to think that gold had more of the element fire in it compared to iron, because gold is not only shinier but maintains its lustre longer.

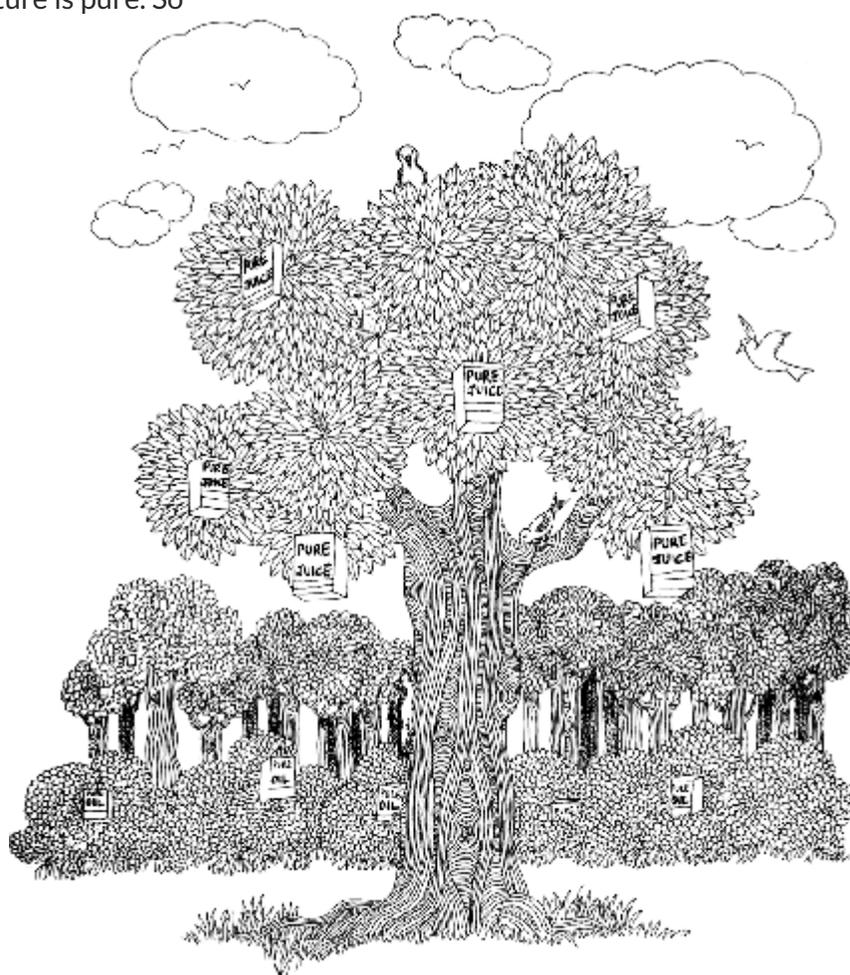
When it came to metallurgy, they explained the process as obtaining a compound – the metal – from the elemental ore – calx. We now know that metals are elements obtained from their ores (compounds) – most commonly oxides, sulphides or carbonates. Why did they get it all wrong? It is because this idea had its basis in the notion we still cherish that everything in nature is pure. So

people thought whatever they got from nature was pure and we add impurities to these pure things in chemical reactions.

This notion persisted because it was never challenged by factual data. Alchemists never thought of measuring how much metal was obtained from a weighed amount of calx. Their primary interest lay in the properties of the products they could obtain, so they seldom measured or paid much attention to how much of a substance they used in their reactions or how much of a new substance was formed. They had no concept of atoms and, like Aristotle, saw matter as continuous, so they believed one substance could combine with another in any proportion whatsoever. They used arcane symbols to depict metals and common compounds, using them as a kind of shorthand in their diagrams and procedures.

But there was also another side to alchemy that was more in line with practices in modern chemistry (see box: ANOTHER SIDE TO ALCHEMY).

*It is a common belief that all the things we obtain from nature are pure*



## Another side to alchemy

In pursuing their metaphysical quests the alchemists came up with many useful discoveries and perfected many experimental techniques that helped the later development of modern chemistry. Among them was the Arab Abu Musa Jabir ibn Hayyan (considered by many to be the father of chemistry) who developed an early experimental method around 770 AD and isolated several acids including hydrochloric, nitric, citric, acetic and tartaric acid.

There were also the Siddhas of Tamil Nadu in South India, whose philosophy was developed during the period from 200 BC to 1200 AD. These yogic-poets were adept in the science of healing and alchemy and preserved their insights into material substances and healing practices in verse. In addition, *Rasaratnakara*, a treatise attributed to Nagarjuna in the 10th century AD, dealt with preparations of mercury (*rasa*) compounds but also talks of extraction of metals from their ores.

Spanish alchemist Pseudo Geber was one of the first to describe nitric acid around 1310 AD and proposed the theory that all metals are composed of various proportions of sulphur and mercury, while Paracelsus is said to have laid the foundations of pharmaceutical chemistry around 1530 AD.

## Boyle is the sceptical chemist who refutes the metaphysical ideas of the alchemists

The Persian chemists Abu al Rayhan al Biruni and Avicenna (around 1000 AD) were among the earliest to question the practices of alchemists and their theory of transmutation of metals. But it was left to Robert Boyle (1627-1691) to draw the line between chemistry and alchemy in his epoch-making book *The Sceptical Chymist*, which many people see as the beginning point of the history of modern chemistry. The British scientist is often referred to as the 'father of modern chemistry'. He delineated chemistry as we know it today, separating pharmacy (the preparation of medicines and drugs) from metallurgy and other applications.



Boyle observed the huge changes in volume exhibited by gases

Another scientist who played a key role in refuting the claims of alchemists was the French chemist Antoine-Laurent Lavoisier (1743-1795), who, incidentally, is also considered by many to be the founder of modern chemistry.

The alchemists claimed that water could be transmuted into soil by removing its wetness – water was seen to have the properties of wetness and heaviness whereas soil had the properties of dryness and heaviness. They distilled water to a high level of purity to get dryness that would result in the formation of 'soil'. And it appeared as if they were successful.

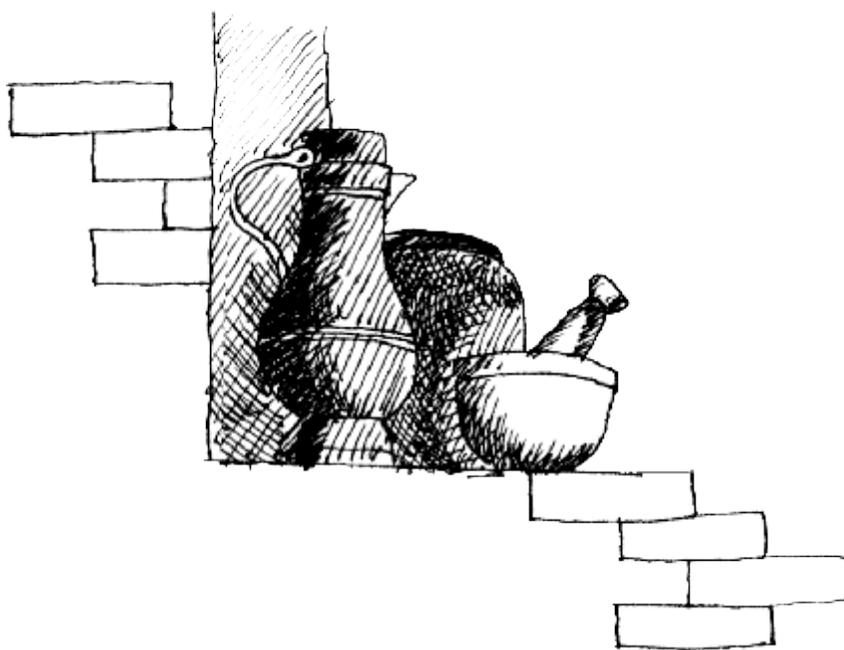
Lavoisier repeated their experiment to conclusively prove that no transmutation had taken place, tracing the 'experimental error' to the variety of glass used in the apparatus – which was slightly soluble in water. The French chemist accurately weighed the apparatus before and after the distillation to show that the amount of 'sand' produced was accounted for by the loss in weight of the glass, thus refuting the alchemists' claim.

Another key alchemical conclusion that Lavoisier proved to be erroneous was in an

experiment to obtain mercuric oxide by heating mercury. In those days, a known amount of mercury would be placed in a closed vessel and heated from outside using lenses. The mercuric oxide obtained was then weighed. The weight of the mercuric oxide formed was generally found to be less than the initial amount of mercury used in the experiments.

The alchemists explained this apparent loss of weight as the result of impurities being removed from the impure metal to give the pure, elemental calx! The real explanation is far simpler. When mercury is heated with a lens, the high temperature generated causes some of the mercury to evaporate and deposit on the walls. This deposit was never weighed.

Lavoisier repeated the experiment to show that if the deposit is heated gently, we get back the original mercury. He concluded that the deposit is a compound of metal and oxygen, weighing the metal and deposit to show that their combined weight is greater than that of the original metal. The experiment also led him to conclude that air itself is a mixture and not an element, with one-fifth (oxygen) combining with the metal while four-fifths did not.



## Lavoisier lays the ground for quantification and the discipline of stoichiometry

One practical reason for the absence of quantification in chemical experiments in those days was the lack of equipment to accurately measure weights. There was also no way of collecting or measuring the gases involved or formed in a reaction. In fact, gases didn't even figure in experimental observations because they were not considered to be part or product of a reaction. Even after people started measuring weights of reactants and products in a rudimentary manner (only solids or liquids, because there was still no way of collecting gases), these ideas continued to go unchallenged largely because of the kinds of reactions that were being studied by the alchemists.

It was Lavoisier who revolutionised the science of chemistry with his experimental techniques and his quantitative chemical analysis, which laid the ground for the discipline of stoichiometry. He perfected apparatus to collect all the products of a reaction, including gases, and devised instruments that could weigh substances with a high degree of accuracy.

He carried out his reactions in closed systems,

meticulously measuring all the matter he started out with and all the matter he ended up with, including 'invisible' matter that floats away in gaseous form (probably the first person to do so) to show that the sum total of matter is the same.

The sum total of matter was also shown to remain the same in the case of physical changes, such as when water boils and turns to steam or cools to become ice. The particles of water continue to exist in the vapour or in ice and return to liquid form when cooled or heated.

This important principle – that matter cannot be created or destroyed in a chemical reaction or physical change – is today enshrined in Lavoisier's law of conservation of mass, which he formulated in 1774 in his *Traite elementaire de chimie* (For another important contribution to chemistry see box: LAVOISIER ON FIRE AND PHLOGISTON). The law states that during a chemical reaction the weights of the reactants and products are equal (However, today we know that nuclear reactions can turn matter into energy, resulting in a difference of the weights measured before and after the reaction).

## Lavoisier on fire and phlogiston

One of Lavoisier's important contributions to chemistry was his explanation of combustion and respiration in terms of oxygen consumption. Fire represented one of the earliest symbols of chemical change – altering food through cooking, transforming substances like metals through smelting, etc. So fire and combustibility played an important part in chemical theories from ancient times. Fire was one of the four basic elements of the early Greek philosophers while sulphur, the principle of combustibility, was an elementary principle of the alchemists.

But 18th century chemistry was dominated by the phlogiston ('burning up') theory of combustion. First stated in 1667 by Johann Joachim Becher (1635-1685) and developed into a theory by Georg Ernst Stahl (1660-1734) in 1703, it postulated the existence of a 'fire-like' element called phlogiston. Metals were composed of phlogiston and calx and burning resulted in the loss of phlogiston. The problem was that some metals gained weight during combustion, so phlogiston was said to have negative weight to explain this gain. It was also seen that combustion somehow decreased the volume of air. The English chemist Joseph Priestley (1733-1804), a supporter of the phlogiston theory, put this decrease down to the 'goodness' of air.

Lavoisier couldn't accept anything as

illogical as negative weight, so he performed a series of experiments to test the theory. He showed that air has two components, one that lights up a burning candle and another that extinguishes it.

When an object is burned in a closed environment, the fire-supporting part is reduced, leaving behind part which does not support combustion. So in all cases of combustion where an increase in weight was observed, Lavoisier concluded that a part of air had been absorbed, while in cases where calx was burned with charcoal, this part was released. So combustion was essentially a process in which there is a chemical union between the burning substance and a part of air which he identified as oxygen. And in the case of burning calx, it results in the release of oxygen.

Lavoisier extended his explanation of combustion to respiration as well, showing that oxygen is consumed and carbon dioxide given off.

His experiments also disproved another assumption of the phlogiston theory – that calx or 'earths' were simple bodies and metals were obtained from them by adding phlogiston. Lavoisier showed that metals are actually simple bodies and calx is obtained by their reaction with oxygen.

## More insights into matter

***As astronomers discover that everything in the universe is made of matter, scientists work out new laws to show how matter behaves in chemical reactions***

Our understanding of matter had begun to change from the time of Newton, who first came up with the idea that matter resisted change in its motion, and the degree to which an object resisted (its inertia) being its mass. In the fourth edition of his *Optics*, published posthumously in 1730, he talks about matter being formed “in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to space... (that) may compose bodies of one and the same nature and texture”. Further insights into matter in the 17th century came from astronomers who began to realise that the same laws govern matter on earth as well as in space, showing that everything everywhere is made up of matter.

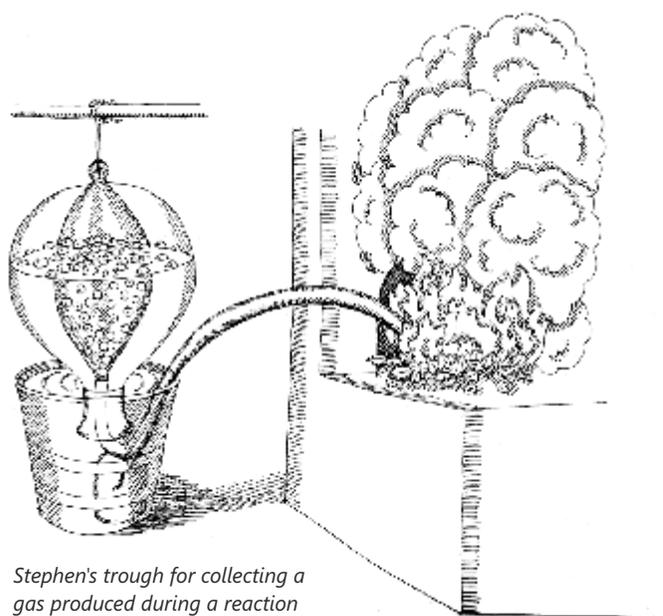
Equally important for the evolution of ideas and growth of scientific knowledge were the development of experimental techniques and the increasing availability of scientific apparatus and equipments during the period (see box: HOW SCIENTIFIC KNOWLEDGE ACCUMULATES AND GROWS: THE CONCEPT OF VACUUM AND THE DISCOVERY OF ARGON).

That was the time when the work of Boyle provided insights into the particulate nature of matter. Using the vacuum pump (invented by Otto von Guericke in 1645) and the pneumatic trough (used for collecting gases), he studied how the volume of a gas varied when the pressure on it was increased or decreased. He found an interesting underlying pattern in the compression/expansion of gases: their volume is inversely proportional to the pressure applied on them at constant temperature ( $V \propto 1/p$ ).

Building on the Greek idea of atoms he suggested (in 1738) that the compression/expansion of gases as well as the change in volume when a liquid turns into a gas was the result of particles of matter moving apart or closer together, increasing or decreasing the empty space between them.

The Swiss physicist David Bernoulli (1700-1782) also used the idea of particles in motion to explain the behaviour of pressurised gas, relating the heat of the gas to the accelerating motion of the particles.

Incidentally, Boyle was also the first scientist to give us a working definition of elements, which was later refined by Lavoisier into a very practical definition (see box: THE EVOLVING DEFINITION OF ELEMENTS).



*Stephen's trough for collecting a gas produced during a reaction*

## How scientific knowledge accumulates and grows: the concept of vacuum and the discovery of argon

The evolution of ideas and the growth of scientific knowledge depends crucially on the experimental techniques and scientific apparatus and equipments available during any period. We give two examples to illustrate this: first, how the concept of a vacuum evolved, and, next, the story of the discovery of argon, a noble gas.

Aristotle believed that no void could exist naturally since nature abhors a vacuum. This idea withstood the challenge of time for hundreds of years until the 17th century, when the Italian physicist Evangelista Torricelli (1608-1647) conducted his vacuum experiments to become the first scientist to create a sustained vacuum and discover the principle of the barometer. He filled a four-foot long glass tube with mercury and inverted the tube in a dish. Most of the mercury flowed out of the tube into the dish but some did not escape, creating what Torricelli argued was a vacuum at the top of the tube, thus posing the first serious challenge to the prevailing Aristotelian notion.

Torricelli built the first mercury barometer in 1644 when he realised that changes in atmospheric pressure from day to day caused variations in the height of mercury in a tube.

The invention of the vacuum pump was the next step in gaining more insights into vacuum, with Otto von Guericke (1602-1686) conducting his famous Magdeburg hemispheres experiment to show that teams of horses could not separate two hemispheres from which air had been pumped out.

Incidentally, the predecessor of the vacuum pump, the suction pump, was known from the time of the Romans in Pompeii (during the 1st century AD) as well as the Arabs in the 13th century.

Boyle improved the design of the vacuum pump with help from Robert Hooke (1635-1703) to conduct his experiments on the properties of vacuum.

The story of the discovery of argon is no less interesting. The first hint of the existence of this gas came through the investigations of air conducted by the English scientist Henry Cavendish (1731-1810) in 1785. He was interested in finding out more about the fraction of air that was not oxygen. He knew that nitrogen could react with oxygen to form nitrogen oxides. He used an electric spark to react oxygen with nitrogen in air, adding more oxygen to ensure that all the nitrogen had reacted. Since nitrogen oxides are acidic, he used aqueous sodium hydroxide to remove them and then used potassium polysulphides to remove the remaining oxygen. To his surprise, he found a small bubble of gas remaining. He wrote that this bubble "was not more than one hundred and twentieth of the bulk of the phlogisticated air (nitrogen)". However, he did not proceed further to investigate this inert bubble.

Not much attention was paid to this little nugget of information until more than a hundred years later. In 1892, English physicist John William Strutt (1842-1919), who was investigating the atomic weights of oxygen and nitrogen, announced that oxygen is

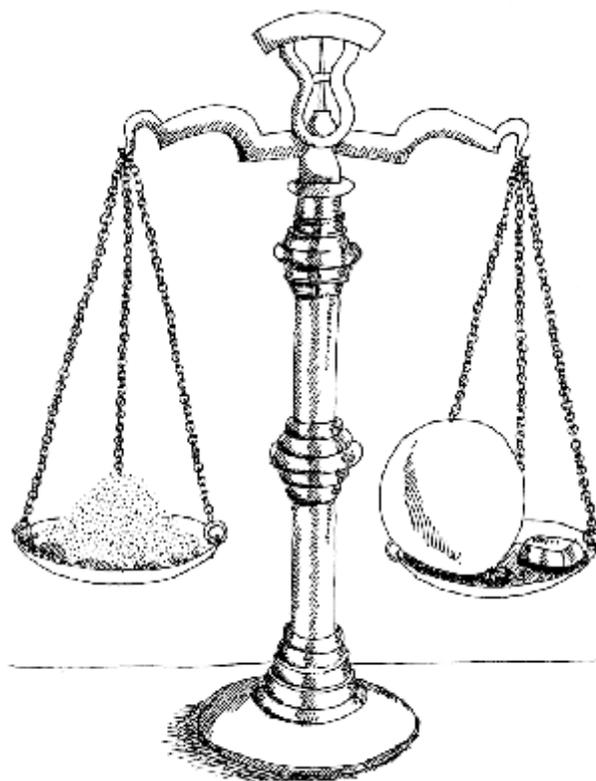
always 15.882 times denser than hydrogen, regardless of how it is prepared, basing his observation on the experiments he had conducted. However, when he tried to find the atomic weight of nitrogen he found that nitrogen in air is always denser by about 0.5 times than nitrogen formed in chemical reactions. He could not find an explanation for this discrepancy, asking for suggestions in a letter sent to the journal *Nature*.

The challenge was taken up by British chemist William Ramsay (1852-1916) who repeated Cavendish's experiment, removing all the components of air – oxygen, carbon

dioxide and nitrogen. He then went a step further because he had an advantage over Cavendish – access to spectroscopic techniques that were not available during Cavendish's time. He heated the remaining bubble of gas and studied the spectral lines emitted and found that they did not fit any known element. The new gaseous element, which was completely inert and made up about 1% of the atmosphere, was named 'argon' in a joint paper he wrote with Strutt in 1895 to announce the discovery, for which they received the Nobel Prize in 1904. Argon comes from the Greek 'argos', which means inactive or lazy.

The stage had now been reached in the history of chemistry where the number of elements was much more than the five conceptualised by Aristotle and we had a rule to recognise different elements. We also had the concept of the particulate nature of matter to explain what happens when a substance changes state, or when fluids mix, and why gases are compressible.

Most important was the quantitative turn chemistry had taken with Lavoisier's work. Scientists were meticulously measuring weights of substances taking part or being produced in reactions and trying to make sense of the numbers obtained. They paid special attention to ensure that they could balance the weights of the materials they started out with in a chemical reaction with the weights of the products of the reaction. This carefully collected data later helped chemists to devise simple new laws about the behaviour of matter in chemical reactions.



*The total amount of products is equal to the total amount of the reactants*

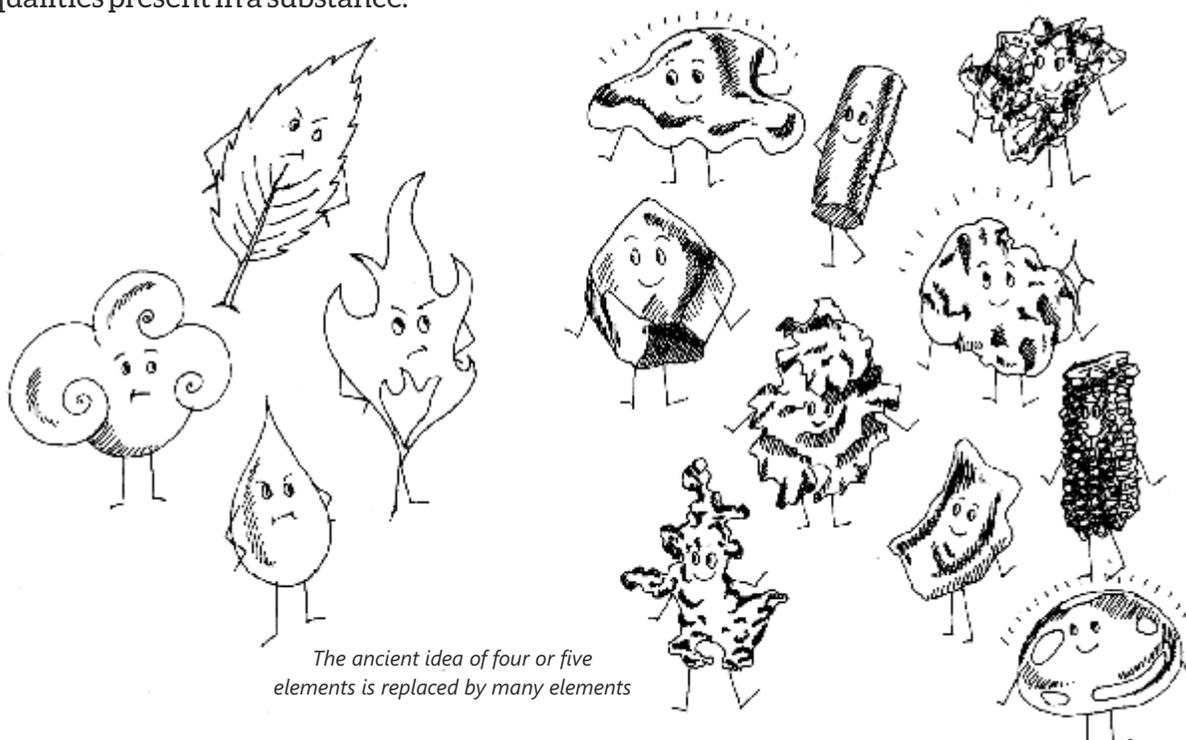
The law of conservation of mass was one of three laws that added to our understanding of the nature of matter during this period. The other two were the law of reciprocal proportions articulated by Jeremias Benjamin Richter (1762-1807) sometime between 1792 and 1794, and the law of constant (or definite) proportions formulated by the French chemist Joseph Proust (1754-1826) in 1799. Both Richter and Proust benefited from the quantitative turn that chemistry had taken and the vast amounts of data now available to them from the carefully monitored experiments of many chemists.

The law of constant proportions was derived after analysing many compounds and their compositions. It states that compounds always contain elements in a definite proportion. What this means is that whatever method you use to prepare a compound or whatever the source of your starting materials, you always end up with the same proportion of elements in that compound. (Also see boxes: UNDERSTANDING THE LAW OF CONSTANT PROPORTIONS; THE BURNING CANDLE AND THE LAW OF CONSTANT PROPORTIONS; AND OUT OF DISPUTE COMES KNOWLEDGE).

## The evolving definition of elements

Aristotle and other early philosophers tried to define elements solely by reason. Boyle and other later scientists used the results of numerous experiments to identify the elements. Boyle was the first to move away from the Greek idea of elements representing the various qualities present in a substance.

The concept of 'chemical element' developed slowly in 17th and 18th centuries to be operationally defined as a substance that cannot be separated into different components by known methods.



*The ancient idea of four or five elements is replaced by many elements*

The modern story of elements begins in 1661 with Boyle, who defined an element in the following words in his book *The Sceptical Chymist*: “I now mean by elements, as those chemists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixed bodies are immediately compounded, and into which they are ultimately resolved.”

Put simply, it means an element is a substance that cannot be decomposed into simpler substances by chemical processes. It also states that chemical compounds are made up of these elements and a compound can be decomposed into its constituent elements by chemical means. This definition provided a practical way to distinguish between elements and compounds. However, it did not get enough attention for over a century.

Around a hundred years later in 1789, Lavoisier built on Boyle's definition to give us a working definition of an element in the preface of his *Traité Élémentaire de Chimie* (Elements of Chemistry): “If we apply the term elements, or principles of bodies, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. Not that we are entitled to affirm, that these substances we consider as simple may not be compounded of two,

or even of a greater number of principles; but, since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation has proved them to be so.”

Both Boyle and Lavoisier thus define an element as any substance that cannot be broken down into simpler constituents. As Lavoisier points out, this also implies that any list of elements at any given time in history would reflect the methods of analysis and separation available at that time. This is clearly seen in the list of chemical elements he published, which includes some elements that are now known to be compounds, such as metallic oxides and salts. But they were accepted as elements at the time because they could not be decomposed by any method then known.

The important thing is that Lavoisier's list encouraged the adoption of standard names for the elements. This systematised nomenclature also ensured that compounds were named from their constituent elements. Prior to this, many of the names used for different substances verged on the trivial, being based on their place of origin, appearance or smell. Sometimes one substance was known by different names. We still use some of these names, such as milk of magnesia. Lavoisier's contribution ensured that different people could be sure they were talking about the same substances.

## Understanding the law of constant proportions

Here is an example to help you understand what is being said in the law of constant proportions:

100g of mercuric oxide decomposes to give 92.6g of mercury and 7.4g of oxygen, 10g of oxygen reacts with 125g of mercury while 10g of mercury reacts with 0.79g of oxygen to give mercuric oxide. Do these values agree with the law of constant proportions?

What we need to do is check if the proportion of mercury and oxygen combining to give mercuric oxide is the same in all three cases. The simplest way to do this is to see how much of one element reacts with 1g of the other element in each case.

In the first case, 100g of mercuric oxide decomposes to give 92.6g of mercury and 7.4g of oxygen - i.e. 7.4g of oxygen requires 92.6g of mercury. Therefore, 1g of oxygen requires  $92.6/7.4$  of mercury = 12.5g of mercury.



*The amount of oxygen required by a given amount of mercury is always in a fixed proportion*

In the second case, 10g of oxygen reacts with 125g of mercury, i.e. 10g of oxygen requires 125g of mercury. Therefore, 1g of oxygen requires  $125/10$ g of mercury = 12.5g of mercury.

In the third case, 10g of mercury reacts with 0.79g of oxygen, i.e. 0.79g of oxygen requires 10g of mercury. Therefore, 1g of oxygen requires  $10/0.79$ g of mercury = 12.6g of mercury.

The proportion of oxygen to mercury in all three cases are:

1:12.5  
1:12.5  
1:12.6

Hence we can say the law of constant proportions is being obeyed within the limits of experimental error.

We can also solve this problem by calculating how much oxygen reacts with 1g of mercury in each case.

In the first case, 100g of mercuric oxide decomposes to give 92.6g of mercury and 7.4g of oxygen, i.e. 92.6g of mercury requires 7.4g of oxygen. Therefore, 1g of mercury requires  $7.4/92.6$ g of oxygen = 0.079g of oxygen.

In the second case, 10g of oxygen reacts with 125g of mercury, i.e. 125g of mercury requires 10g of oxygen. Therefore, 1g of mercury requires  $10/125$ g of oxygen = 0.08g of oxygen.

In the third case, 10g of mercury reacts with 0.79g of oxygen, i.e. 10g of mercury requires 0.79g of oxygen. Therefore, 1g of mercury requires  $0.79/10$ g of oxygen = 0.079g of oxygen.

The proportion of mercury to oxygen in all three cases are:

1:0.079  
1:0.08  
1:0.079

Here again we see that the law of constant proportions holds: we can calculate it by taking a constant weight for either of the two elements involved.

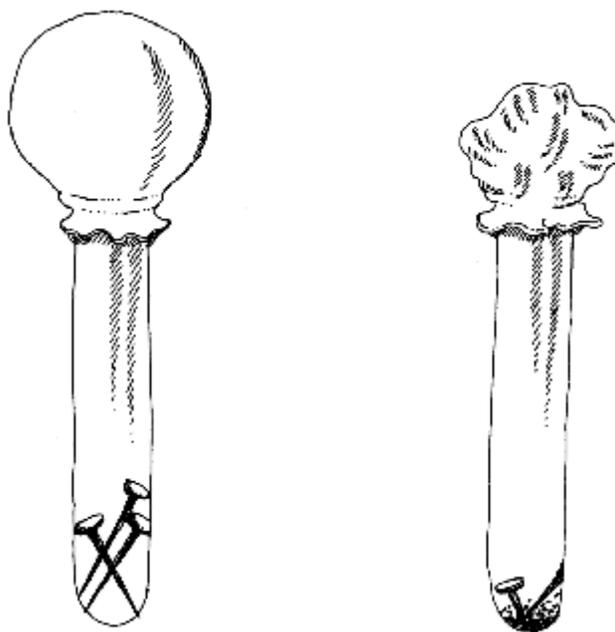
Try and solve the two problems given after this to see if you have got the hang of the law of constant proportions.

**Problem 1:** Copper oxide can be decomposed to give 11.2% oxygen and 88.8% copper. How much copper will react with 32g of oxygen? (Solve this by assuming the law of constant proportions is valid.)

**Problem 2:** Aluminium chloride contains 20.2% aluminium and 79.8% chlorine. If 30g of aluminium reacts with 30g of chlorine, will both materials be completely consumed in the reaction? If not, which one will be left over and how much of it will remain unreacted?

## The burning candle and the law of constant proportions

Does the law of constant or definite proportions give you a hint to explain why a candle extinguishes after some time if covered with a glass, and why it burns longer if covered with a gas jar? The wax in the candle requires oxygen in the air to burn. When the limited amount of oxygen available is fully consumed, it cannot burn any longer. The same is the case when iron is kept in closed containers of various sizes for different periods of time, since rusting occurs in the presence of oxygen and moisture. In the case of the iron left out in the open to rust, we can assume the amount of iron is the limiting factor, i.e. unlimited oxygen and water are available for the reaction to take place. So, the longer you leave the iron out, the more it will corrode. If left out long enough, all the iron will be reduced to rust.



*A portion of air is used up when iron rusts*

## Out of dispute comes knowledge

The law of constant proportions was firmly established as a result of a dispute between Proust, who formulated the law, and French chemist Marcellin Berthollet (1827-1907), who championed the law of chemical affinity, which says that substances combine in variable and indefinite proportions according to the relative concentrations of the reactants. Proust showed that two substances may combine to form more than one compound, but their proportions are always fixed in each compound. It was fortunate for the progress of chemistry that a simple rule was first established. This helped chemists to look for regular patterns in the bewildering variety of reactions around them. However, it is also a fact that non-stoichiometric compounds have since been identified (for example, rust). They are called 'berthollides' in honour of the man who championed their cause.

The law of reciprocal proportions states that if a given weight of an element A combines with a certain weight of element B, and the same weight of A combines with a certain weight of element C, then there should be a definite relationship between the weights of B and C when they combine. They should either be in the same ratio as they each bear to A, or some integral multiples of those weights.

Here is an example to further clarify the point:

1g of A combines with 'x'g of B  
1g of A combines with 'y'g of C

Now, if B and C combine, the weight ratio would be:

'x'g of B combines with 'y'g of C  
or 'x'g of B combines with 'n × y'g of C  
or 'n × x'g of B combines with 'y'g of C

where n is a small whole number.

(Also see box: UNDERSTANDING THE LAW OF RECIPROCAL PROPORTIONS)

## Understanding the law of reciprocal proportions

Let us look at an example that illustrates this law.

On analysis, sodium hydroxide is seen to contain 95.8% sodium and 4.2% hydrogen by weight. On the other hand, when water decomposes, it gives 11.2% hydrogen and 88.8% oxygen by weight. On the basis of this data and applying the law of reciprocal

proportions, what will be the proportion in which sodium and oxygen combine to give sodium oxide?

Both sodium and oxygen react with hydrogen. From the data given, we have to find the proportion in which they combine to give sodium oxide. As in the case of the example given in the law of constant

proportions, we shall simplify matters by figuring out how much sodium and oxygen react separately with 1g of hydrogen.

From the data given, sodium hydride contains 95.8% sodium and 4.2% hydrogen by weight, i.e. 4.2g of hydrogen reacts with 95.8g of sodium. Therefore, 1g of hydrogen reacts with  $95.8/4.2$ g of sodium = 22.8g of sodium.

Water contains 11.2% hydrogen and 88.8% oxygen (by weight), i.e. 11.2g of hydrogen reacts with 88.8g of oxygen. Therefore, 1g of hydrogen reacts with  $88.8/11.2$ g of oxygen = 7.9g of oxygen.

According to the law of reciprocal proportions, if 22.8g of sodium reacts with 1g of hydrogen to give sodium hydride and 7.9g of oxygen also reacts with 1g of hydrogen to give water, then if sodium and oxygen react, the proportion in which they react will be:

22.8g of sodium to 7.9g of oxygen

This compares well with the formula of sodium oxide ( $\text{Na}_2\text{O}$ ) and the atomic weights of sodium and oxygen. That is,  $\text{Na}_2\text{O}$  contains 44.98g of sodium and 16.0g of oxygen, or 44.98g of sodium:16.0g of oxygen.

According to our calculations:

22.8g of sodium:7.9g of oxygen

or

45.6g of sodium:15.8g of oxygen

Appendix 2 gives a series of practice problems that should help students develop a better appreciation of the laws of chemical combination.

Hence, we can see how the law of reciprocal proportions applies in this case. This law has limited applicability because there are only a few substances that combine with each other and also with a third substance. However, it can be applied to a chain of substances and the weights of different elements combining with each other can be calculated. These weights are called equivalent weights.

Some equivalents calculated by Jeremia Benjamin Richter with 1,000 parts of sulphuric acid as the standard are given below:

Bases		Acids	
Alumina	525	Fluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Muriatic (HCl)	712

Now try the problem given below to verify the law:

**Problem 3:** Fluorine and oxygen combine to form a fluoride whose weight-percentage composition is 70.5% fluorine and 29.5% oxygen. Water decomposes to give 11.2% hydrogen and 88.8% oxygen by weight. Apply the law of reciprocal proportions to get the amounts of fluorine and hydrogen that react to give hydrogen fluoride.

## Atomic theory

***Dalton introduces a new kind of logic to work out his seminal ideas about the particulate nature of matter and usher in a new chapter in the history of chemistry***

By the end of the 18th century, we had three laws that were universally applicable to chemical reactions – the laws of conservation of mass, constant proportions and reciprocal proportions. But what made these laws valid? What accounted for their universal applicability in chemical reactions? Why did elements combine in definite proportions? Why couldn't they combine in random proportions? What made it possible to predict how an element would react with another? Why was it easier to predict the reaction if we knew how the two elements reacted with a third element?

Boyle and Bernoulli had hinted at a possible explanation with their idea that matter is made up of particles. But it was the English chemist John Dalton (1766-1844) who provided a workable and pragmatic explanation that wove this idea into a logical framework. The atomic theory he proposed in the early years of the 19th century used a different kind of logic to explain chemical reactions, ushering in a new chapter in the history of chemistry.

Like other researchers of his time, the English chemist benefitted from the increasing quantification of chemical reactions. New apparatus made it possible to collect gases and new equipments such as refined weighing scales made it possible to accurately measure each component of these reactions.

Writing in his *A New System of Chemical Philosophy* in 1808, Dalton said: “These observations have tacitly led to the conclusion which seems universally adopted, that all bodies of sensible magnitude, whether liquids or solid, are constituted of vast number of extremely small particles, or atoms of matter bound together by a force of attraction, which is more or less powerful according to circumstances.”

“...This conclusion, which appears completely satisfactory;...we have hitherto made no use of it, and that the consequence of the neglect has been a very obscure view of chemical agency...” he added, decrying the fact that Boyle's work had been overlooked for so long.



*Dalton gave us the idea of atoms which was based on experimental data*

Dalton had an advantage over Boyle: he knew about the universal applicability of the laws of conservation of mass and constant proportions. This data helped him to go a step ahead of his predecessor and observe: "Whether the ultimate particles of a body, such as water, are all alike, that is, of same figure, weight, etc, is of some importance. From what is known we have no reason to apprehend a diversity in these particulars... Now it is scarcely possible to conceive how aggregation of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others, if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observation may be made on other substances. Therefore we may conclude that the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water and every particle of hydrogen is like every other particle of hydrogen, etc."

This simple paragraph is among the most profound and far-reaching statements written about the nature of matter. It contains two postulates of Dalton's atomic theory:

- All matter is made up of particles.
- All particles of a substance are alike.

Dalton examined chemical change in terms of these particles, using Lavoisier's definition of an element as a substance that is "the last point which analysis is capable of reaching" to conclude that there was a unique atom for each element. "Chemical analysis and synthesis go no farther than to the separation of particles one from another and their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to



*Dalton's explanation of the laws of chemical combination support Boyle's suggestion that matter is particulate*

create or destroy a particle of hydrogen. All changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance", he wrote.

This is the third important postulate of his atomic model, that matter cannot be created or destroyed during a chemical reaction and a chemical change is basically a rearrangement of particles. These particles are atoms. In any chemical combination, decomposition or any other type of reaction, atoms just separate from their partners in the starting material and rearrange themselves to give the products. No new atom of any element is created nor is any atom of an element destroyed.

To sum up, Dalton saw atoms as solid, indivisible particles with no inner spaces. They could not be seen, touched, or tasted and they were indestructible, preserving their identities in all chemical reactions, with each element having its own specific atom that was different from the atoms of other elements. Given this model of matter (see box: DALTON'S ATOMIC THEORY IN A NUTSHELL), the laws of chemical combination become obvious.

## Dalton's atomic theory in a nutshell

The postulates of Dalton's atomic theory can be summarised as follows:

- All matter is ultimately composed of atoms that can neither be subdivided nor changed into another.
- Atoms can neither be created nor destroyed.
- All atoms of the same element are identical, having the same weight, size, shape and other properties.
- The atoms of a given element are different from those of any other element.
- The atoms of different elements can be distinguished from one another by their respective relative weights.
- Atoms of one element can combine with atoms of other elements to form chemical compounds.
- Chemical change is the union or separation of atoms as a whole, the reaction simply changing the way the atoms are grouped together. So atoms always combine in whole number multiples of each other, for example, 1:1, 1:2, 2:3, 1:3 and so on.



*Postulates of Dalton's atomic theory*

## Dalton's atomic theory paves the way for the law of multiple proportions

Dalton's atomic explanation also led to a change in the way chemists reported their data. Earlier, the elements or compounds taking part in a reaction and their products were given as percentages. This caused some problems. Take the example of the two oxides of copper known at the time. One of them, red oxide, contains 89% copper and 11% oxygen by weight. The other, black oxide, contains 80% copper and 20% oxygen by weight. This data gives no hint about any relationship between these different weights.

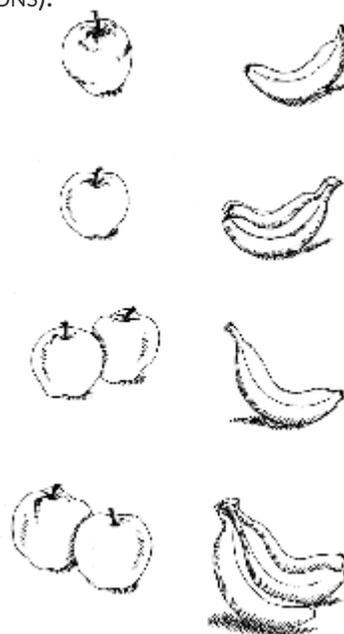
The situation changes if the data is represented as mass ratios. The mass ratios of copper and oxygen in the two oxides are 89:11 and 80:20 respectively (simplified to 9:1 and 8:2). It immediately becomes apparent that for a fixed amount of copper (that is say, 1g), the amount of oxygen required is in the ratio 1:2 (for 1g of copper, 0.123g and 0.25g respectively). So reorganising the data can give fresh insights to discern a new pattern (law).

This is the law of multiple proportions that Dalton was able to predict from his atomic theory. The law states that if two elements combine to form more than one compound, then the ratio of the weights of one element combining with a fixed weight of the other will be in small whole numbers. The law proved to be universally true as the data available in chemical literature was reorganised.

This predictive power of the atomic theory arises from the postulate that atoms cannot be subdivided. That is, if two elements A and B react to form more than one compound, then the molecules of the compounds must be made up of:

1 atom of A + 1 atom of B or,  
1 atom of A + 2 atoms of B or,  
2 atoms of A + 1 atom of B or,  
1 atom of A + 3 atoms of B or,  
2 atoms of A + 3 atoms of B and so on.

So you will definitely not find compounds of A and B having half atoms of A or B, and since the weights of the atoms of each element are fixed, the law of multiple proportions is self-evident (Also see box: UNDERSTANDING THE LAW OF MULTIPLE PROPORTIONS).



*If we picture the atoms of one element as apples and the atoms of another element as bananas, then they could combine in various ways*

## Understanding the law of multiple proportions

Let us look at a couple of examples of the law to understand it better:

Carbon burns in excess oxygen to give carbon dioxide, which is 27.3% carbon by weight and 72.7% oxygen by weight. In insufficient oxygen, it gives carbon monoxide, which is 42.9% carbon by weight and 57.1% oxygen by weight. What is the ratio of carbon combining with the same amount of oxygen?

We need to calculate the amount of carbon combining with the same amount of oxygen (say 1g) to give carbon dioxide and carbon monoxide and see if these two amounts are in a simple ratio.

In carbon dioxide: 100g of carbon dioxide contains 27.3g carbon and 72.7g oxygen, i.e. 72.7g of oxygen reacts with 27.3g of carbon. Therefore, 1g of oxygen reacts with  $27.3/72.7$ g of carbon = 0.38g of carbon.

In carbon monoxide: 100g of carbon monoxide contains 42.9g carbon and 57.1g oxygen, i.e. 57.1g of oxygen reacts with 42.9g of carbon. Therefore, 1g of oxygen reacts with  $42.9/57.1$ g of carbon = 0.75g of carbon.

The amounts of carbon reacting with 1g of oxygen to give carbon dioxide and carbon monoxide are in the ratio 0.38:0.75, which can be simplified to 1:2.

Now calculate the ratio of oxygen combining with the same amount of carbon to give these two compounds.

Also, solve the following problems:

**Problem 4:** Fluorine and oxygen combine to form a fluoride whose weight composition is 70.5% fluorine and 29.5% oxygen. These two elements also combine to produce a second fluoride whose weight composition is 54.2% fluorine and 45.8% oxygen. Show how this data confirms the law of multiple proportions.

**Problem 5:** Sodium combines with oxygen in two distinct chemical combinations. The products of these two reactions are given below:

- Sodium oxide: 74.2% sodium, 25.8% oxygen
- Sodium peroxide: 59.0% sodium, 41.0% oxygen

How does this data illustrate the law of multiple proportions?

## Calculating atomic weights

**Dalton makes some wrong assumptions in his singular obsession that nature works in simple ways but his work points the way to deciphering chemical reactions**

In addition to explaining the laws of chemical reactivity, Dalton's theory also helped further the concept of atomic weights. In the third postulate of his theory, he says that atoms are matter and so have weight, and the atoms of the same element have the same weight. Since weight is a measurable quantity, he tried to calculate the atomic weights of different elements on the basis of the composition of various compounds. He had to make some assumptions in order to do so since he knew it was impossible to weigh individual atoms.

He first assigned a weight of 1 for hydrogen since it was the lightest element known: when any compound containing hydrogen decomposes the lowest yield in terms of its weight percentage is hydrogen. The atomic weights of all other elements were calculated relative to hydrogen.

Dalton knew from experimental data that a definite amount of an element combines with a definite amount of second element. But he had

no idea about the number of atoms contained in these amounts of each element. Once again, take the example of copper and oxygen, which react to produce two different compounds. What was clear to Dalton was that the amount of oxygen in one compound was double the amount in the second compound. But what wasn't obvious was whether this represented one atom of oxygen in one compound and two in the other or two in the first and four in the second, or so on. It was also not clear whether the atom/atoms of oxygen combined with one or more atoms of copper.

So Dalton had to assume the formula of each compound in order to assign atomic weights to its constituent elements. He had faith in simplicity, which meant that nature would not complicate matters and confuse us, so he assumed that elements would combine in one-to-one ratios. This meant that if a compound is formed from the elements A and B, it would have the formula  $A_1B_1$  — one atom of A with one atom of B. (Also see box: THE WEIGHT OF ASSUMPTIONS)

## The weight of assumptions

There are reasons to believe that Dalton could have solved the enigma of atomic weights had he not been so caught up with his idea of simplicity. At times he even tended to reject experimental data in favour of his cardinal faith in simplicity. That's what happened to Joseph Louis Gay-Lussac's data, which Dalton rejected on the ground of coincidence and experimental error. We must remember that Gay-Lussac (1778-1850) was widely respected for his tremendous experimental skills, unlike Dalton himself, who was not a very good experimentalist.

We have seen that Dalton's assumption about simplicity did not hold water, ironically in the case of water itself. 'Simplicity' led him to assign the formula HO to water and he calculated the atomic weight of oxygen as 6.5, which he later raised to 7. Continuing to work on the 'simplicity' assumption, Humphry Davy

(1778-1829) raised it to 7.5 and, ultimately, Joseph-Louis Proust (1754-1826) arrived at the 'correct' figure of 8.

Dalton then turned to the oxides of carbon and nitrogen to calculate the atomic weights of other elements. The possible choices he faced are shown in the table below. One oxide of carbon had a C/O ratio of 0.75:1 and the other had a ratio of 0.375:1. So if one oxide was CO (which Dalton assumed) the other would be CO<sub>2</sub>. Or they could be C<sub>2</sub>O and CO. The first possibility gives carbon an atomic weight of 6. If the second possibility is accepted, the atomic weight would be 3. Dalton found the first oxide was more stable on decomposition, so he assumed its formula as CO, which was the correct choice in hindsight.

Similarly with the oxides of nitrogen, Dalton ruled out possibilities 1 and 3 below, because a molecule made up of five

Oxides of Carbon	C/O Mass ratio	Possibility 1	Possibility 2
Oxide 1	3/4	CO	C <sub>2</sub> O
Oxide 2	3/8	CO <sub>2</sub>	CO
Atomic weight of carbon	assuming oxygen=8	6	3

Oxides of Nitrogen	N/O Mass ratio	Possibility 1	Possibility 2	Possibility 3
Oxide 1	3 ½ /8	NO	NO <sub>2</sub>	NO <sub>4</sub>
Oxide 2	7/8	N <sub>2</sub> O	NO	NO <sub>2</sub>
Oxide 3	14/8	N <sub>4</sub> O	N <sub>2</sub> O	NO
Atomic weight of nitrogen	Assuming oxygen=8	3 ½	7	14

atoms clashed with his doctrine of simplicity. So nitrogen was assigned an atomic weight of 7.

But then he came to ammonia. Going by simplicity he assumed its formula to be NH. Since 42/3g of nitrogen combine with 1g of hydrogen, this assumption gives the atomic weight of nitrogen as 42/3, which conflicts with the value of 7 obtained from the nitrogen oxides data.

Dalton could have changed tack and worked out ammonia's formula taking the atomic weight of nitrogen as 7. This would have given him a molar ratio of 1:0.667 for hydrogen/nitrogen for an  $N_2H_6$  formula or any of its multiples (like  $N_4H_{12}$ ). But his faith in simplicity remained unshaken.

However, one should not underestimate Dalton's efforts. We need to appreciate the

problems chemists faced in the early 19th century. One should remember that in 1808 he had no alternative way of ascertaining molecular formulae. Some assumptions had to be made and he took recourse to his rule of simplicity, which served well enough in many cases. Although it proved to be incorrect, the assumption definitely provided a way to describe bulk reactions in atomic terms.

**Problem 6:** The following exercise should give you a better insight into assumptions and their consequences. First, determine the relative weights of the atoms in each compound, assuming that the formulae are correct and the atomic weight of hydrogen is 1. Then calculate the atomic weights applying the rule of simplicity while assuming the formulae of the different compounds.

COMPOUND	% COMPOSITION BY WEIGHT
HCl	2.74% hydrogen, 97.26% chlorine
NaCl	39.3% sodium, 60.7% chlorine
$Na_2O$	74.15% sodium, 25.85% oxygen
$CO_2$	27.3% carbon, 72.7% oxygen
$CS_2$	15.80% carbon, 84.20% sulphur
$H_2S$	5.9% hydrogen, 94.1% sulphur

If two compounds of A and B are formed, then one (generally the more abundant) would be  $A_1B_1$  and the second would be either  $A_2B_1$  (two atoms of A with one atom of B) or  $A_1B_2$  (one atom of A with two atoms of B), depending on the relative weight percentages of A and B obtained on decomposition of these compounds.

Dalton rounded off the figures he got for the weights of atoms of elements to ensure that they were mostly whole numbers.

Let's take a specific example that illustrates the procedure he followed to calculate the atomic weight of oxygen. Water was the only compound of hydrogen and oxygen known at the time, so Dalton assumed a formula of HO for water on the basis of his rule of simplicity and calculated the atomic weight of oxygen from the available decomposition data of water. The data showed that water contained 87.5% oxygen and 12.5% hydrogen by weight. So the atomic weight he calculated for oxygen was 7:

$$\frac{\text{Mass of Oxygen}}{\text{Mass of Hydrogen}} = \frac{\text{Mass Ratios of Bulk Amounts } 87.5}{12.5} = \frac{\text{Mass Ratios of One Atom each } 7.0}{1.0}$$

This is less than half the accepted weight of oxygen, which is to be expected since Dalton assigned HO as the formula for water instead of  $H_2O$ . But nature is not always so simple and elements often combine in ratios other than one-to-one. That's why many of Dalton's weights turned out to be incorrect as seen in the table below. However, his work still represented a big step forward.

(For some practice problems in calculating atomic weights, see box: CALCULATING ATOMIC WEIGHTS).

ATOMIC WEIGHTS CALCULATED BY DALTON	
Element	Relative Atomic Weight
Hydrogen	1
Carbon	5.4
Phosphorus	9
Iron	50
Copper	56
Azote (Nitrogen)	5
Oxygen	7
Sulphur	13
Zinc	56
Lead	95

## Calculating atomic weights

You can also try your hand at calculating atomic weights. Note the importance of assuming a formula and the difficulties faced by Dalton in this regard while you do these problems.

**Problem 7:** On analysis, sodium hydride is seen to contain 95.8% sodium and 4.2% hydrogen by weight. What is the atomic weight of sodium if the formula of sodium hydroxide is NaH and hydrogen is taken as the standard with a weight of 1?

**Problem 8:** Water is 11.2% hydrogen and 88.8% oxygen. Calculate the atomic weight of oxygen assuming hydrogen as the standard with an atomic weight of 1. First, calculate the atomic weight of oxygen assuming the formula of water is HO, as Dalton did. Then calculate the atomic weight with the correct formula of water ( $\text{H}_2\text{O}$ ) and compare your answer with the atomic weight of oxygen given in the modern periodic table.

## The study of gaseous reactants and their products by Gay-Lussac and Berzelius provides more pointers

The early 19th century was also the time when many chemists began studying gases. As pointed out earlier, this component of chemical reactions was generally overlooked because of the lack of equipment to collect the gases generated. As the equipment became available, investigations into gases gathered steam, providing new insights into atomic theory as well as our understanding of chemical formulae.

Among those who conducted many experiments to study how gases reacted and combined was the French chemist Joseph Louis Gay-Lussac. Unlike Dalton, who noted the weights of the reactants and products in a chemical reaction, he studied the volumes of reacting gases. For example, he would say three litres of hydrogen react with one litre of nitrogen to give two litres of ammonia. In the same case Dalton would say 3g of hydrogen react with 14g of nitrogen to give 17g of ammonia. The point of interest is that

while weights appeared to increase by simple addition on combination, volumes could increase or even decrease at times.

Gay-Lussac formulated a law in 1809 based on his observation that gases combine in simple proportions by volume at a given pressure and temperature and, if the products are gaseous, they also bear a simple whole number ratio to the gaseous reactants. Some volume and weight ratios of reacting gases are on the next page.

Two years later in 1811, Italian physicist Amedeo Avogadro (1776-1856) proposed a hypothesis that pointed to a distinction between gases composed of simple units (atoms) and complex units (molecules). Unfortunately, Avogadro's work was ignored for 40 years for two reasons. First, he lived in Italy while the centres of activity in chemistry at the time were France, Germany, Britain and Sweden. The second reason was that

### Volume and Weight ratios of some reacting gases

Reaction components	Gas volume ratio of reactants	Weight ratio of reactants
Hydrogen + Oxygen $\rightarrow$ Water	2:1	01:08
Hydrogen + Chlorine $\rightarrow$ Hydrogen chloride	1:1	01:35
Carbon monoxide + Oxygen $\rightarrow$ Carbon dioxide	2:1	28:08
Methane + Oxygen $\rightarrow$ Water + Carbon dioxide	1:2	16:32

most chemists of the time were not prepared to accept the concept of molecules because they could not imagine that a molecule could contain atoms with similar 'affinities' (scientists were not talking about electric charges in atoms at that point of time).

It was left to Jöns Jacob Berzelius (1779-1848) to bring some order to the confusing and sometimes contradictory quantitative experimental data. The Swedish chemist, who did a lot of work on calculating atomic weights of various elements between 1808 and 1826, was familiar with the work of both Dalton and Gay-Lussac.

Taking the example of chlorine, which reacts with hydrogen to form hydrogen chloride, he applied Dalton's logic of simplicity to the combination – a binary comprising one atom of hydrogen and one atom of chlorine. In accordance with Gay-Lussac, the gas volume ratio of hydrogen and chlorine in combination would be 1:1.

Since Dalton also proposed that atoms combine in simple whole numbers to give compounds,

then a given volume of say, 1,000 hydrogen atoms would combine with 1,000 atoms of chlorine. Since this amount of chlorine occupies the same volume as hydrogen, it follows that equal volumes of any gas would contain the same number of atoms under the same conditions of temperature and pressure. So, if one litre of hydrogen reacts with one litre of chlorine, this volume of each gas would contain an equal number of atoms, otherwise they would not react completely.

His reasoning pointed to a link between integral ratios of volumes and integral ratios of weights. So if the densities (g/L) of different gases under identical conditions of pressure and temperature are measured, they would be proportional to their atomic weights. For example, if one litre of gaseous element A weighs 'x'g and one litre of gaseous element B weighs 'y'g, the ratio x:y will be the ratio of their atomic weights because one litre of each gas will contain the same number of atoms. The table below gives the atomic weights of some gaseous elements calculated on the basis of their densities, using hydrogen as the standard:

Name of gas	Density (g/L)	Relative Atomic Weight (Density of given gas / Density of hydrogen)
Hydrogen	0.08987	$0.08987/0.08987=1$
Nitrogen	1.2507	$1.2507/0.08987=13.9$
Chlorine	3.212	$3.212/0.08987=35.7$
Oxygen	1.429	$1.429/0.08987=15.9$

The table below compares the atomic weights obtained by Dalton's 'proportional weight' method with those calculated by the gas density method:

Element	Atomic Weight	
	Dalton's Method	Gas Density Method
Hydrogen	1 (by convention)	1 (by convention)
Nitrogen	5	13.9
Oxygen	7	15.9

The results are clearly conflicting. This confusion led many scientists of the time to decry atoms and atomic theory as causing more trouble than they were worth!



*Chemists thought the idea of atoms to be not just confusing, but of no help in explaining phenomena*

## Dalton has problems with Berzelius' method but the confusion is about molecules

As we have seen, determining atomic weight depended on two things – the number of atoms of combining elements in compounds and their weights. For example, one atom of zinc combines with one atom of oxygen to give zinc oxide. By measuring the relative weights of zinc and oxygen in the compound, one gets the relative weights of the atoms of each element. (The combining ratio is the weight of the oxide minus the weight of the metal divided by the weight of the metal. So if the oxide has two atoms of oxygen to one of the metal, then the ratio must be divided by 2.)

Berzelius standardized the atomic weights of all gaseous elements to that of oxygen, assigning a value of 100 to it. He described the steps to determine the atomic weight of chlorine relative to oxygen and to hydrogen in his *Treatise on*

chemistry: "I established its (chlorine's) atomic weight by the following experiments: (1) From the dry distillation of 100 parts of anhydrous potassium chlorate, 38.15 parts of oxygen are given off and 60.85 parts of potassium chloride remain behind (Good agreement between the results of four measurements). (2) From 100 parts of potassium chloride 192.4 parts of silver chloride can be obtained. (3) From 100 parts of silver 132.175 parts of silver chloride can be obtained. If we assume that chloric acid is composed of 2 Cl and 5 O, then according to these data 1 atom of chlorine is 221.36. If we calculate from the density obtained by Lussac, the chlorine atom is 220 (relative to the atomic weight of oxygen). If it is calculated on the basis of hydrogen, then it is 17.735." (Also see box: CHANGING STANDARDS FOR CALCULATING ATOMIC WEIGHTS).

## Changing standards for calculating atomic weights

Atomic weight is the ratio of the average mass of an atom of an element compared to a standard unit. Since atoms are too small to measure, chemists in the 19th century (beginning with Dalton) determined the atomic weights of different elements in relative terms – as multiples of the atomic weight of hydrogen, the lightest element, which was assigned a value of 1. The atoms of other elements were compared against this standard to calculate their atomic weights.

But there was a problem in using hydrogen as the standard. If refinements in measurements through improved techniques led to a better value for the weight of hydrogen, even a small change would cause the atomic weights of other elements to change by a large factor. Berzelius suggested using oxygen as the standard assigning it with an atomic weight of 100. But this unit never really caught on.

Oxygen was, however, a good choice for a standard since it reacts with most other elements and so the relative weights can be calculated directly for many elements. So it was used as the standard from around 1900 to 1961 with an assigned value of 16. So the unit of atomic weight was defined as  $1/16$  the weight of an oxygen atom.

However, when isotopes were later discovered, it was found that the relative atomic weights of elements also reflected the percentage composition of their isotopes. Two other isotopes of oxygen were discovered – O-17 and O-18, making it unsuited to serve as a standard.

Eventually in 1961, a new scale was established based on the carbon-12 atom, the most abundant isotope. The definition of atomic weight then became  $1/12$  the weight of the carbon-12 atom. This is the standard that is currently in use.

The result is half the modern values. The reason lies in the distinction between atoms and molecules. We must remember that the concept of 'molecule' was unknown at the time and 'atom' was used to describe the ultimate particle of both elements and compounds, with Dalton using the term 'compound atom' to describe the smallest particle of a compound made up of atoms of two or more elements. Hydrogen exists as a molecule made of two atoms of hydrogen. So the standard would be  $2H = 1$ , which is what Berzelius understood, giving an atomic weight for chlorine of 17.735 relative to hydrogen.

The lack of an understanding of molecules and atoms gave rise to another problem. If Berzelius' conclusion that equal volumes of gases contained equal numbers of atoms was correct, it meant the atoms were splitting during some chemical reactions. Let's again consider the example of hydrogen chloride. One litre of hydrogen and one litre of chlorine combine to give two litres of hydrogen chloride gas. According to Berzelius, this would mean that one atom of hydrogen and one atom of chlorine give two atoms of hydrogen chloride.

1 litre of hydrogen + 1 litre of chlorine  $\rightarrow$  2 litres of hydrogen chloride

or (according to Berzelius)

1 atom of hydrogen + 1 atom of chlorine  $\rightarrow$  2 atoms of hydrogen chloride

so

$\frac{1}{2}$  atom of hydrogen +  $\frac{1}{2}$  atom of chlorine  $\rightarrow$  1 atom of hydrogen chloride



*Dalton could not accept Berzelius's explanation of Gay-Lussac's data*

One atom of hydrogen chloride having half an atom each of hydrogen and chlorine! That was something Dalton could never accept since he was convinced that atoms cannot be split. So he rejected the work done by Gay-Lussac, claiming that the observation that gases reacted in simple volume ratios was either sheer coincidence or due to experimental error.

There is an irony in the situation. Berzelius is known today for having taken measurements of gaseous reactants to a new level of accuracy and precision. He had a reason for doing so. He wanted his data to fit the requirements of Dalton's atomic theory, which placed strict conditions on the combination of different

elements to form compounds. As we have seen, Dalton used hydrogen as a standard, calculating atomic weights of elements as multiples of its atomic weight. However, Berzelius' investigations ended up revealing that the atomic weight of some elements falls between two multiples of the hydrogen weight. (Today we know this is because of isotopes of these elements. See the earlier box on changing standards for calculating atomic weight.) He published a table of atomic weights in 1826 that mostly shows good agreement with modern values (given in the next page). He analysed over 2,000 compounds, and also calculated the weights of 43 elements.

Incidentally, Berzelius also developed a system of chemical notation in which each element was assigned a simple written label – O for oxygen, Fe for iron, etc – with proportions written in numbers. This is the system we use today, the

only difference being that Berzelius superscripted the numbers showing the number of atoms of each element ( $H^2O$ ) while we subscript them ( $H_2O$ ).

Element	Berzelius atomic weights (1826)	Modern atomic weights (1983)
Hydrogen	0.998	1.008
Carbon	12.25	12.01
Nitrogen	14.16	14.01
Oxygen	16.00	16.00
Sulphur	32.19	32.06
Chlorine	35.41	35.45
Calcium	40.96	40.08
Sodium	46.54	22.99
Iron	54.27	55.85
Chromium	56.29	52.01
Copper	63.31	63.54
Potassium	78.39	39.10
Strontium	87.56	87.62
Iodine	123.00	126.90
Barium	137.10	137.34
Gold	198.88	196.97
Mercury	202.53	200.59
Lead	207.12	207.19
Silver	216.26	107.87

## Specific heat provides another way to calculate atomic weights and determine formulae

The technique to do this was worked out by French chemist Pierre Louis Dulong (1785-1838) and French physicist Alexis Therese Petit (1791-1820). While investigating Dalton's idea that the heat capacity of the atoms of gases was related to their sizes, they found many of his hypothetical figures were wrong. They also noticed an important relation between atomic weight and specific heat, proposing (in 1819) that the amount of heat (measured in calories) required to raise the temperature of a single atom of a solid by a given amount is independent of the type of atom. So the heat required to raise the temperature of 1g atomic weight of any solid element by 1°C would be a constant (because 1g atomic weight of all elements contains the same number of atoms). According to their law of atomic heat, the constant is approximately equal to 6.4cal/°C:

$$\text{specific heat} \times \text{atomic weight} = 6.4\text{cal}/^{\circ}\text{C}$$

so

$$\text{atomic weight} = 6.4/\text{specific heat}$$

Since the specific heat could be determined experimentally, this law could be used to find the approximate atomic weights of metals. Some values obtained by Dulong and Petit are given in the table below. They were also able to spot some errors in Berzelius' atomic weights, as in the case of silver.

(\*The unit for specific heat used was cal/g°C, but modern SI system uses J/gK. If the SI units are used, the constant will be 25 instead of 6.4.)

The following example shows how this law can be used to decide between different formulae of compounds:

Metal	Specific heat (cal/g°C)	Atomic weight
Bismuth	0.0288	222.2
Gold	0.0298	214.8
Platinum	0.0317	201.9
Tin	0.0514	124.5
Zinc	0.0927	69.0
Gallium	0.088	72.7
Copper	0.0949	67.4
Nickle	0.1035	61.8
Iron	0.1100	58.2
Calcium	0.1498	42.7

If 1.074g of silver oxide is formed from 1.000g of silver, what is the formula of the compound formed between silver and oxygen, and what is the atomic weight of silver, if the approximate atomic weight of silver, calculated from its specific heat, is 113.3 and the atomic weight of oxygen is 16.

The weight of silver in 1.074g of silver oxide is 1.000g.  
The weight of oxygen in 1.074g of silver oxide is 0.074g.

Therefore, the mass ratio of silver and oxygen is:  
 $1.000/0.074 = 13.51$ .

Assuming the formula of silver oxide to be Ag<sub>2</sub>O, this means an atom of silver is 13.51 times heavier than an oxygen atom. Since the atomic weight of oxygen is 16, the relative atomic mass of silver in silver oxide is  $16 \times 13.51 = 216.16$

From the specific heat data, we have the approximate atomic weight of silver as 113.3, which is roughly half the weight obtained above. Hence, the formula of silver oxide is Ag<sub>2</sub>O and the

atomic weight of silver is  $216.16/2 = 108.08$ , which compares well with the accepted value for the atomic weight of silver.

The following table compares atomic weights of some elements obtained by the three methods discussed above. But there was no way of deciding between the values!

Atomic weights are given relative to hydrogen, although Berzelius used oxygen as the standard.

Element	Atomic weight (Dalton)	Atomic weight (Berzelius)	Atomic Weight (Specific heat)
Hydrogen	1*	1*	
Iron	50		58.2
Copper	56		67.4
Nitrogen	5	13.9	
Oxygen	7	15.9	

## Cannizzaro revives Avogadro's ideas to conclude the long story of atomic weights

Unfortunately, the Dulong and Petit method was not adopted until the 1850s because the two scientists gave no explanation for the regularity they found. So chemists felt it was just as speculative as Dalton's rule of simplicity.



*If we have one crate of apples weighing 10 kg and another of bananas weighing 15 kg, and if we count and find that the number of apples and bananas is the same, we can find out the weight of apples relative to the weight of bananas*

The basic problem in determining atomic weights lay in extrapolating macroscopic measurements of some amount of an element, comparing it with an amount of another element and then drawing conclusions about the relative masses of individual atoms. Such comparisons are valid only if we are dealing with the same number of atoms of each of these elements. For example, if we have a box of bananas weighing 15 kg and a box of apples weighing 10 kg, it would only be valid for us to say that each banana is one and a half times as heavy as an apple if we know that each of them contains a dozen of each fruit. With bananas and apples, it would be simple enough to open the box and count. But while dealing with atoms, the problem is that we cannot count them.



*If the crates are closed, and we cannot count the number of apples and bananas, we would not be able to find out their relative weights*

But then atomic weights are a useful measure because they give us a way to interpret our macroscopic measurement in terms of the number of atoms taking part in reactions. Ultimately, resolving the problem of determining atomic weights was a triumph of logic and one of the foundations of modern chemistry. Things were finally sorted out due to the contributions of Avogadro and the Italian chemist Stanislao Cannizzaro (1826-1916).

Let us take a closer look at Avogadro's work, which was overlooked during the time Berzelius conducted his investigations. The Italian physicist presented a totally new model of gases while trying to reconcile Dalton's atomic theory with Gay-Lussac's experimental results. There was no clear concept of molecules at the time, so confusion reigned when it came to deciding how many atoms of each element combined in a compound.

Now take a second look at Gay-Lussac's data. When we worked with weights, we saw that it was simple arithmetic to say that the total weight of the reactants was equal to the total weight of the products. However, gases do not behave in such a simple manner when their volumes are measured. For example, if two litres of hydrogen and one litre of oxygen are mixed without bringing them in contact with a spark, the volume of the mixture would equal the combined volume of the two gases – three litres. So physical mixing of gas volumes is additive. But if a spark is introduced in the mixture and the gases react, the volume reduces and measures only two litres provided the water formed remains in the gaseous state. This discrepancy puzzled everyone in those days.

## Avogadro, molecules and caloric

A puzzle looking for a rational explanation during Avogadro's time was the behaviour of matter in different states. Why did a substance occupy a larger volume in its gaseous state compared to its liquid or solid state? While Dalton's atomic theory gave pointers to the behaviour of gases in chemical reactions, it could not explain physical changes in a substance from the solid and liquid to the gaseous phase, except in terms of atoms moving closer or further away from each other.

One view prevalent at the time was that particles in gases were in contact but the cohesive force between them was weak. It was thought that each particle was surrounded by a substance called caloric (heat), which kept them apart. So heating an object meant adding more caloric around the particles. Dalton assumed that all atoms of an element had the same amount of caloric but the amount differed for atoms of different elements. So the distance between particles of different gases would differ. By implication, this meant equal volumes of different gases would contain different numbers of particles.

Now read what Avogadro had to say in presenting his model to reconcile Dalton's theory with Gay-Lussac's experimental results: "It is very well conceivable that molecules of gases being at such a distance that their mutual attraction cannot be exercised, their varying attraction for caloric may be limited to condensing a greater or smaller quantity around them, without the atmosphere formed by this fluid having any greater extent in any one case than the other,

and consequently without the distance between the molecules varying; or in other words, without the number of molecules contained in a given volume being different."

What his explanation showed is the possibility that equal volumes of all gases contain an equal number of particles.

Going on from there to tackle the problem of Gay-Lussac's results, he says: "We suppose that the constituent molecules of any simple gas are not formed of a solitary atom, but are made up of a certain number of these atoms united by attraction to form a single one; and further that when molecules of another substance unite with the former to form a compound molecule, the molecule splits up into two or more parts (or atoms) composed of half, quarter, etc, parts of molecules and combine with half, quarter, etc, of the second substance so that the number of integral molecules of the compound becomes double, quadruple, etc, [than] what would have been if there had been no splitting up, and exactly what is necessary to satisfy the volume of the resulting gas."

Finally, he adds: "Dalton, on arbitrary supposition as to the most likely relative number of molecules in a compound, has endeavoured to fix ratios between the masses of molecules of simple substances. Our hypothesis, if well founded, puts us in a position to confirm or rectify his results from precise data, and, above all, to assign the magnitude of compound molecules according to the volumes of the gaseous compounds, which depends upon the division of molecules entirely unsuspected by this physicist [Dalton]."

Given Dalton's atomic theory and Gay-Lussac's law of combining volumes, Avogadro saw a relation between the occurrence of simple ratios in the volumes of combining gases and the number of molecules in them. Incidentally, Avogadro talked of 'compound molecules' and 'primary molecules'. He postulated that elemental gases may exist as compound molecules having an even number of primary molecules (molecules of elements) – 2, 4, 6. He further stated that equal volumes of all gases, at the same temperature and pressure, contain an equal number of molecules.

This was a bold new idea. Avogadro was proposing that even elements could exist as molecules, which he called constituent (or primary) molecules. This meant the data for the reaction between hydrogen and chlorine that bothered Dalton could be explained as follows:

1 litre of hydrogen + 1 litre of chlorine  $\rightarrow$  2 litres of hydrogen chloride

According to Avogadro this meant:

n molecules of hydrogen + n molecules of chlorine  $\rightarrow$  2n molecules of hydrogen chloride  
1 molecule of hydrogen + 1 molecule of chlorine  $\rightarrow$  2 molecules of hydrogen chloride  
 $\frac{1}{2}$  molecule of hydrogen +  $\frac{1}{2}$  molecule of chlorine  $\rightarrow$  1 molecule of hydrogen chloride

Assuming each molecule of hydrogen contains 2 atoms of hydrogen and each molecule of chlorine also contains 2 atoms of chlorine, one molecule of hydrogen chloride could be produced in the following manner:

1 atom of hydrogen + 1 atom of chlorine  $\rightarrow$  1 molecule of hydrogen chloride

Avogadro's excellent suggestion was ignored by other chemists for two reasons. First was

isolation. He worked in Italy at a time when much of the chemistry was being done in Germany and France, so few people came across his work. More importantly, chemists could not see any reason why atoms of the same element should combine with each other to form molecules. Chemical reactions were explained as taking place between elements having opposite properties. Hence sodium and potassium would react with chlorine, but not with each other.

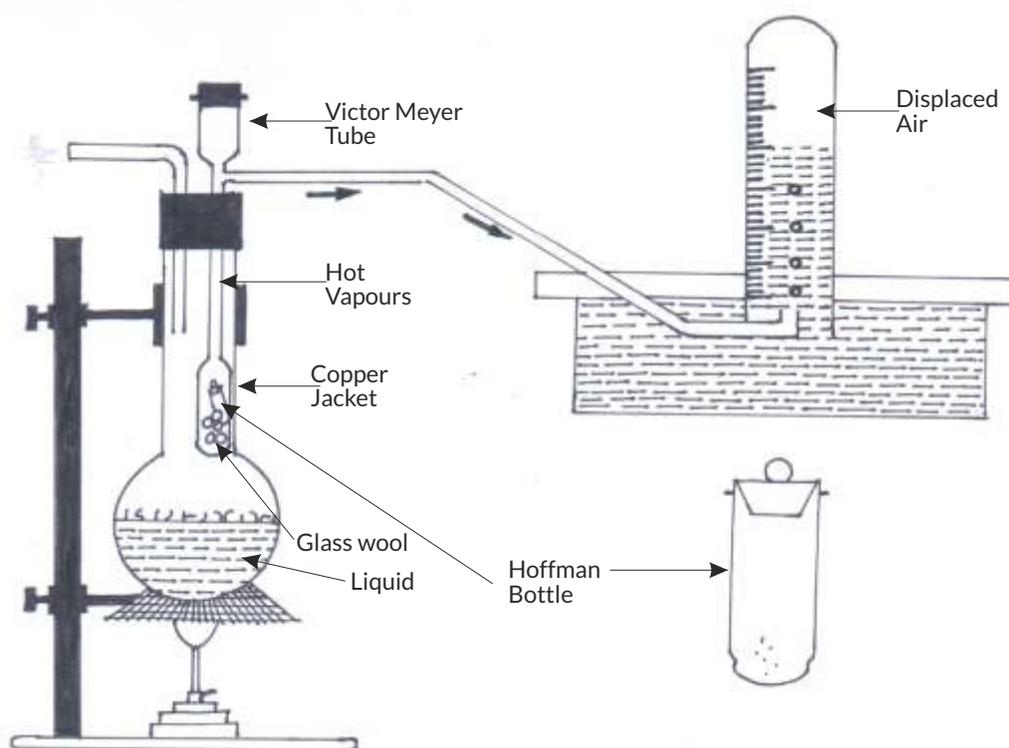
However, matters were finally resolved by Stanislao Cannizzaro (1826-1910) who rediscovered Avogadro's hypothesis and devised a method to calculate atomic weights based on it. He explained how one volume of oxygen could form two volumes of water without violating the theory that atoms are indivisible, using Avogadro's explanation that molecules of gases, such as hydrogen and oxygen, existed as diatomic molecules (molecules with two atoms joined together). If the oxygen molecule was composed of two oxygen atoms, it was the molecule and not the atom that split to form two volumes of water.

In his method (see Appendix 1), he first determined the number of atoms of an element per molecule of the element. Next, he determined the relative molecular weights from the gas densities of as many gaseous or vaporisable compounds of that element as could be prepared. Analysing these compounds, he found the smallest weight of the element contained in the molecular weight of the various gaseous compounds of the element. This smallest weight was accepted as the relative atomic weight of an atom of the element. Stated as a law, it says that the different quantities of the same element contained in different molecules are all whole multiples of the atomic weight. (Also see box: CALCULATING MOLECULAR WEIGHTS FROM VAPOUR DENSITIES).

## Calculating molecular weights from vapour densities

Avogadro's hypothesis suggests a method to determine molecular weights. If equal volumes of different gases always contain an equal number of molecules, then the molecular weights are proportional to the densities of the gases. The German chemist Victor Meyer (1848-1897) devised a method in 1878 to determine the vapour densities of liquids. A weighed quantity of the liquid is evaporated in a tube at a constant high temperature. The air displaced by the vapour is collected and cooled to room temperature

after which its volume is measured. This equals the volume of the vapourised liquid. The weight of the liquid used, divided by the volume of the vapour in litres, gives the vapour density. The molecular weight is obtained by multiplying the vapour density of the liquid by the molecular weight of air. Meyer took the molecular weight of air to be 28.73, assuming that air is 14.367 times heavier than hydrogen. He added that the number 28.95 should be used instead of 28.73, if the molecular weight of oxygen is taken as 16.



Cannizzaro outlined his method in a pamphlet 'Sketch of a course of chemical philosophy', which was distributed at the first international congress of chemists that was held in Karlsruhe (Germany) in 1860 to resolve issues related to determining atomic weights and the difference between 'atom' and 'molecule'.

His theory was accepted because it appeared to be the best way to resolve the confusions arising out of the different methods of calculating atomic weights. He was helped by the fact that a large number of carbon compounds were known by that time, with different numbers of carbon atoms linked to one another in these compounds.

That made 'molecules of elements' a more palatable concept even though he could not explain how similar atoms are linked in a compound. It was only in the 20th century that Linus Pauling eventually explained the nature of 'covalent' bonds underlying this phenomenon.

Cannizzaro's method led to calculations of atomic weights that were consistent and gave values close to modern values. The weights of molecules (of elements or compounds) were obtained by adding the weights of the constituent atoms.

(Also see box: MEASURING THE ATOMIC WEIGHT OF OXYGEN).

## Measuring the atomic weight of oxygen

Knowing the atomic weight was vital for finding out the chemical composition of a compound, calculating reacting quantities in chemical reactions and understanding these reactions. But the 'wet chemistry' methods used by chemists in the 19th century were laborious and far less precise than later physical methods – procedures such as filtrations, dissolutions, and recrystallisations. By the early 20th century atomic weights could be determined easily and precisely using sophisticated instruments like the mass spectrometer.

The most important atomic weight that had to be determined was oxygen's. This was because the atomic weights of most elements had to be calculated by synthesis or analysis of their oxides. So the accuracy of the calculations depended on fixing oxygen's atomic weight as accurately as possible. Any small error in this value would be magnified in the case of the heavier elements.

Most chemists of the time tried to determine oxygen's atomic weight by synthesising water from hydrogen and oxygen. But

because of technical difficulties, most chemists measured two of the three quantities – oxygen, hydrogen, water – involved in the reaction and calculated the third on the basis of the law of conservation of mass.

Edward Williams Morley (1838-1923) avoided such assumptions to come up with the most precise 'wet chemical' determination of oxygen's atomic weight in 1895. The American scientist was a skilled experimentalist who was known for his meticulous and precise measurements of various natural constants – chemical compositions, densities, weights, lengths, etc. He developed elaborate apparatus and methods to remove impurities like water vapour and other gas vapours from gas samples to weigh them more precisely. So he was able to get precise measurements of all three quantities, calculating oxygen's atomic weight at 15.892 by two comparisons – water and oxygen and hydrogen and oxygen. He then cross-checked his results with physical methods – measuring and comparing the densities and volumes of hydrogen and oxygen.

## Atomic theory and what happens when solids, liquids and gases change physically

We have seen that a chemical change happens when the atoms in a molecule are moved around or when atoms are added or taken away. On the other hand, the basic chemical structure remains unchanged in a physical change. What changes are densities, pressures, temperatures and other physical properties.

What does atomic theory have to say about solids, liquids and gases? Diagrams in textbooks that depict these three states of matter tend to confuse students. The properties of substances in each of these states are determined by the arrangement of particles (atoms, molecules or ions). The solid state and gaseous state may cause less confusion. In the solid state, the forces between the particles are strong enough to hold them in place, so each piece of the solid maintains its shape and has a definite size. Confusion arises when we consider the behaviour of fine powders, which can be poured like a liquid and take the shape of the container into which they are poured. There are also solid gels. These differences need to be clarified for the students.

In the gaseous state, the forces between molecules are relatively weak. So gaseous molecules have enough energy at ambient temperatures to overcome the intermolecular forces and move apart. When they move apart, they can again be compressed either by increasing the pressure or reducing the temperature.



*It is not simple to classify substances as solids, liquids or gases*

The huge increase in volume when a solid or liquid substance changes to its gaseous state is often not fully appreciated by children. Nor the ease with which temperature and pressure affect the volume of a gas. The experiments given in this module, along with the focused discussions, could help them in arriving at a better understanding of the gaseous state.

The liquid state is often the least understood. Children deal with liquids and solids, so it is assumed that there would be no confusion in their minds about these two states of matters. But like the confusions caused by powders and gels, children are confused by the different liquids they come across and the range of their properties.

For example, they are told that liquids can be poured, but honey is very difficult to pour. The change in volume when a solid turns into a liquid is also often exaggerated. The densities of substances in the solid and liquid states do not differ to the same extent as the densities of the

liquid and gaseous states – when a liquid boils and turns into vapour, the volume increase is in the thousand-fold range.

The main difference between the solid and liquid states of a substance is the long-range order in the arrangement of particles in the solid, which is absent in the liquid. The particles in the liquid state are held together much less firmly and, hence, are free to move within the body of the liquid – therefore, we observe their commonly stated properties, namely that they can be

poured and take the shape of the container into which they are poured.

Change of state is another confusing concept for children. Though they quickly pick up terms like condensation and vaporisation, they are not able to explain the changes taking place at the atomic or molecular level. It needs to be conveyed to them through discussions that the change from solid to liquid and from liquid to gas require the supply of energy while the reverse change results in the release of energy into the surroundings.

## A mole is a very large but convenient number to work with atoms and molecules

The contributions of Dalton, Gay-Lussac, Berzelius, Avogadro and Cannizzarro have given us a robust model of the nature of matter. It tells us that all matter is ultimately made up of particles (either atoms or molecules) and that all particles of a substance are alike and weigh the same. This is the atomic weight in case of atoms and molecular weight in case of molecules. These weights are relative – they tell us how many times a particle is heavier than a particle of hydrogen. So they are only numbers.

In everyday situations as well as in the laboratory, we deal with large amounts of substances. We cannot count the atoms and molecules in the samples we use. So, how do we know how many particles we are handling when, say, we take 10g of common salt? Or when 20g of carbon reacts with, say, 53g of oxygen, how do we know how many atoms of carbon and oxygen are involved in the reaction? The answer lies in Avogadro's theory.

We find his theory (or Gay-Lussac's/Berzelius') gives us another way of looking at the problem – in terms of numbers. Avogadro said equal volumes of gases at the same temperature and

pressure contain equal numbers of molecules. Similarly, Gay-Lussac's results imply that a definite volume of any gas under specific conditions of temperature and pressure would contain the same number of particles as any other gas. We have also seen that equal volumes of two gases like hydrogen and chlorine react completely with each other under those similar physical conditions. Following Dalton's rule of simplicity, this implies that the amounts of the two gases taken would contain the same number of atoms. This number was not known in Dalton's time.

If we take several gases in amounts where their weights equal their molecular weights in grams, we find that they occupy a volume of 22.414 litres at 0°C and 1 atm (Standard Temperature and Pressure – STP) or 24.789 litres at 25°C (298K) and 1 bar (Standard Ambient Temperature and Pressure – SATP). For example, 2g of hydrogen gas and 32g of oxygen gas both occupy a volume of 22.4 litres at STP.

In other words, 22.4 litres of any gas at standard pressure and temperature contain the same number of molecules. The weight of these

molecules is the gram molecular weight (molecular weight expressed in grams). This number is called a mole and is abbreviated as mol. The actual number was calculated much later using several different methods to get its accepted value — 1 mole =  $6.022 \times 10^{23}$ . This number is called the Avogadro number in honour of the man who played an important role in unravelling the mystery about atoms (even though Avogadro himself had no idea of what this number was!)



*Are people talking about me?! – A mole*

It is difficult to imagine how big this number is. Many scientists have tried to illustrate it with graphic examples. For instance, imagine this situation: You fill a test-tube with water (about 1 mole of water) and mark each molecule in some way before mixing it thoroughly in the ocean. You then fill the test-tube with water from the ocean. You will find at least one of your marked molecules in it! An appreciation of just how big this number is would help students understand just how small the particles being talked about are. Compare this number with the present world population, which is just two-thirds of  $10^{10}$ ! Or consider this: It would take 10 billion chickens laying 20 eggs per day more than 10 billion years to lay a mole of eggs!

By extrapolation, we could say that the gram atomic or molecular weight of any substance (solid, liquid or gas) would contain these many particles. If a gas is cooled to its liquid state, and then the solid state, it would still contain the same number of particles and would weigh the same (though only the gas would occupy a volume of 22.4 litres at STP, the solid and liquid states being a lot denser). The mole is a very useful and powerful tool because, using it, we can calculate the number of atoms or molecules of any substance we weigh, if we know its atomic or molecular weight.

Let's take an example:

**The gram molecular weight of water is 18g, i.e. one mole of water weighs 18g. How many moles of water are there in 100 mL of water?**

One mole of water weighs 18g. Since the density of water is 1g/cc, the volume of one mole of water is 18cc or 18mL, i.e. 18mL of water = 1 mol, so 1mL of water =  $1/18$  mol. Therefore, 100mL of water =  $(1/18) \times 100$  mol = 5.55 mol.

100ml of water contains 5.55 moles of water. So when you drink a small glass of water, it means you are drinking  $5.55 \times 6.022 \times 10^{23} = 3.3 \times 10^{24}$  molecules of water! To give you a feel of some of these typical quantities:

- 1 mol of ethanol occupies a volume of 58mL
- 2 mol of iron (112g) is about 1 cubic inch
- A pinch of salt is about  $1/1000$  mol of NaCl
- A drop of water the size of the period at the end of this sentence would contain 10 trillion water molecules.

**Now try solving this problem: The atomic weight of uranium is 238. What is its gram atomic weight? How much would 15 mol of uranium weigh?**

**Atomic theory is accepted by the scientific community and moves several steps ahead, although the end is still not in sight as nature unfolds new mysteries...**

We have seen how thinking on the nature of matter has evolved down the centuries, with each new development building upon previous knowledge. In the modern era of science, this process has essentially been carried forward on the twin pillars of experimentation and mathematics, backed by intuitive thinking, logic and reasoning.

A new scientific theory is not easily accepted. It goes through a process of churning. Many scientists look at it. Some examine the logic of its argument. Others look at what the theory can predict and then see if the predictions are true. Still others point out data that may contradict or question the theory.

By the end of the 19th century, chemists had generated a large amount of data about different elements, how they reacted with each other and in what proportions. They had empirical laws derived from this data as well as theories to show why these laws were valid.

The existence of atoms itself was a hotly debated issue during this time, with several chemists holding the view that chemistry is the art of the possible and one should not worry about fanciful theories. But the end of the 19th century and the beginning of the 20th century saw dramatic proof of the existence of atoms.

German physicist Albert Einstein was among the first to place this conjecture on a firmer footing. In one of the five papers he published in 1905, he

gave a detailed explanation of Brownian motion. He reasoned that small particles (such as pollen grains) moving in a liquid are pushed around in every direction by far smaller atoms of the liquid, and their random motions, though unpredictable, obey certain laws of probability. He proposed statistical/mathematical formulae for these motions and even calculated the number of water molecules per square inch to a high degree of accuracy.

Einstein's work on Brownian motion allowed French chemist Jean Perrin (1870-1942) and others to prove the physical reality of molecules and atoms.

Austrian scientist Josef Loschmidt (1821-1895) had earlier been the first to estimate the size of molecules that make up air (1865). The value he arrived at was twice their actual size but his feat was remarkable, given the approximations he had to make. His method made it possible to estimate the number of molecules in a given volume of gas under standard conditions. Known today as the Loschmidt constant, its modern value is  $2.69 \times 10^{25}$  per cubic metre at STP, a number that is sometimes confused with Avogadro's number in textbooks.

English scientist Michael Faraday (1791-1867) was the first to suggest the existence of a fundamental particle for electricity in 1834, just as the atom is the fundamental particle of an element. Called the 'electron', this particle was discovered by British physicist Joseph John

Thomson (1856-1940) in his cathode ray experiments in 1897. His discovery of this atomic constituent led him to suggest a 'plum pudding' model to describe the structure of the atom in which the electrons were 'plums' floating around in the atomic 'pudding'.

The discovery of the atomic nucleus in 1911 by New Zealand-born physicist Ernest Rutherford (1871-1937) with electrons revolving around it was the next important step in formulating the atomic theory we know today. Danish physicist Neils Bohr (1885-1962) showed that electrons orbit around the nucleus in special orbits called stationary orbits, with different orbits representing different energy levels. The force holding them in orbit was the electrical attraction between negatively charged electrons and positively charged protons.

This led to the 1913 Bohr-Rutherford model, which visualised the atom as a miniature solar system in which the nucleus containing protons was the sun, with electrons orbiting around it like the planets.

It was also seen that the number of electrons in the atom of each element is determined by the number of protons in the nucleus. So an atom with one proton in the nucleus would have one electron in orbit. The analogy between an atom and the solar system breaks down here.

The number of protons in a nucleus, which equals the number of electrons in orbit (except in ionised atoms) is called the atomic number and all atoms that have the same number of protons – the atomic number – are atoms of the same element.

The discovery of the neutron in 1932 by English physicist James Chadwick (1891-1974) showed that the nucleus of an atom contains neutrons in addition to protons. The neutron has no electrical charge but contributes to the stability of the atom and is slightly more massive than the proton, so it adds to the total weight of the atom, called the atomic weight. This weight is the sum of the weights of the protons and neutrons, while

the weight of the electrons is negligible.

By the early 1930s, the Daltonian indivisible atom was resolved into a nucleus made up of protons and neutrons, with electrons orbiting on the outside. So the 'uncuttable' atom was seen to be 'cuttable', with a structure composed of sub-atomic particles. But the story does not end here.

Advances in experimental methods through the 1940s onwards saw the addition of many additional particles – more than the elements contained in the periodic table – existing in nature, some man-made in particle accelerators, some found in cosmic rays.

The concept of quarks, created around 1962, suggested that all these particles are built up of a few of these 'building blocks', leading to the development of the Standard Model of particle physics. The invention of the scanning tunnelling electron microscope in 1981 has even given us 'pictures' of atoms. What next? Will string theory blur the line between matter being particulate or continuous?

The key point about atomic theory is it deals with concepts such as temperature and pressure to describe matter at macroscopic level. In microscopic world, it deals with kinetic motion of atoms to explain macroscopic quantities, which means absorption or transfer of energy.

Chemical reactions involve either the transfer or the sharing of electrons between atoms. Therefore, the chemical reactivity/properties of an element depend on the number of electrons in an atom of that element and the way these electrons bond with electrons of other elements. Protons also play a significant role because the tendency for an atom to either lose, gain or share electrons depends on the charge of the nucleus. But the chemists say the inner structure of atoms belongs to the realm of physics and they deal with chemical reactions only under conditions where atoms are still the ultimate particles!

## Part-2

# Problems in teaching atomic theory

### Misconceptions that students have

Atomic theory lies at the heart of chemistry. In India, the idea that matter is particulate is introduced at the middle school level, before students begin studying chemistry as a separate discipline. This is the age when they struggle to make sense of abstract concepts. The problem is compounded by the fact that they come to school with preconceived notions about matter that may not be in consonance with what is taught. Even with instruction, many of these ideas tend to persist. So many students enter the higher secondary level with this mental baggage.

So what are these misconceptions that have been brought out by several studies of students in different age groups? Let's begin with primary school students. We find that they have a naïve view of matter based on the common sense principle of 'seeing is believing'. So they tend to put powders and gels in categories separate from solids and liquids. They do understand that each substance has a physical state and a solid can melt if heated or a liquid can freeze if cooled. However, they have a problem with gases because these are 'invisible' and because they often don't see gases as matter. And when sugar dissolves in water, they tend to think it 'disappears'. Some may say its 'taste' remains.

Many of these misconceptions, which persist

beyond the primary stage, arise because students tend to see solids and liquids as continuous, not particulate. This is a common sense idea which they find difficult to forsake because they cannot seem to accept the existence of empty space – vacuum – between atoms. They see the space as filled with air, dust, or something else. They also err in estimating the space (distance) between particles in gases, liquids and solids, the separation being grossly overestimated in the case of liquids.

This superficial understanding that matter is continuous makes them assign the bulk properties of the substance to individual particles, attributing macroscopic changes to changes in the shape, size or state of the atoms. So when a substance expands, they believe that the atoms swell and increase in size, or when it melts, they see the atoms melting.

Students at the middle school level are simply unable to grasp what a particle means or conceptualise how it behaves. They cannot grasp that particles have intrinsic motion, nor believe that particles move in liquids, and even solids. Even for extrinsic motion they may believe particles move faster in a heated substance, but may not equate cooling of a substance with a slowing down of particle motion.

## Atomic theory in the classroom

Students begin to develop atomistic ideas as they gain a better understanding of the concept of conservation of substance, weight and volume. However, they still do not easily substitute 'scientific' ideas for the many misconceptions they carry in their minds. A lot depends upon how these abstract concepts that throw light on the nature of matter are treated in school textbooks and how teachers put them across to students.

Existing textbooks tend to treat these concepts in a cursory manner, without going into details or providing evidence of the particulate nature of matter. The diagrams in these textbooks are usually not of much help either and may in fact often convey wrong ideas or mislead students. What compounds the problem is the use of formulae as a symbolic representation of atomic/molecular combinations in various substances, without giving proper explanation.

The result is that atoms remain a mystery for students and they fail to develop an understanding of the implications of atomic theory in describing chemical change or even change in state. They also fail to create a mental picture of the reality represented by abstract symbols.

Let's take a more detailed look at the way atomic theory is dealt with in the classroom. This will help teachers get a better idea of what they need to do if they wish to improve the situation and ensure that learning of this difficult concept is enhanced.

### **Lack of time:**

This is a serious methodological problem. Students are not given sufficient time to assimilate and internalise ideas – many of them counter-intuitive – about the nature of matter. They also do not get enough time to conduct

chemical reactions. With little experience of seeing the mass relationships between the reactants and products, they find it difficult to make connections between events taking place at the bulk scale and their description at the atomic level in the form of formulae and equations.

### **Symbols:**

When talking about matter, teachers tend to constantly shift from the macroscopic (reacting substances) to the sub-microscopic (atoms and molecules taking part in the reaction) to the symbolic (formulae and equations). Textbooks also move between descriptions of macroscopic properties, sub-microscopic properties and the symbol system used to denote them. If these shifts take place without explanation, they tend to confuse students. They must be told which aspects are being discussed and how the different aspects are interrelated.

Take the following example. Students often say that  $\text{N}_2\text{O}_5$  cannot be prepared from  $\text{N}_2$  and  $\text{O}_2$  because you would need three more atoms of oxygen to form the product. The confusion arises because they are unable to realise the relation between the element and its depiction in the form of a symbol/formula. They have no appreciation of how a formula is arrived at. So they tend to merely change the numbers of different atoms in the formula in order to balance equations. They see the activity as a straightforward mathematical exercise instead of something that reflects the exact quantitative nature of the reaction taking place.

### **The problem of gases:**

We have seen that students find it difficult to recognise gases as matter. So they often do not take into account gases that may be used up or produced during a reaction. This gives a

confusing idea about what exactly the chemical reaction is. For example, if the role of oxygen and atmospheric moisture is not recognised in the rusting of iron, students tend to think that iron turning red and crumbly after some time is a property of the metal. They also find it difficult to imagine the vast empty space between particles in gases.

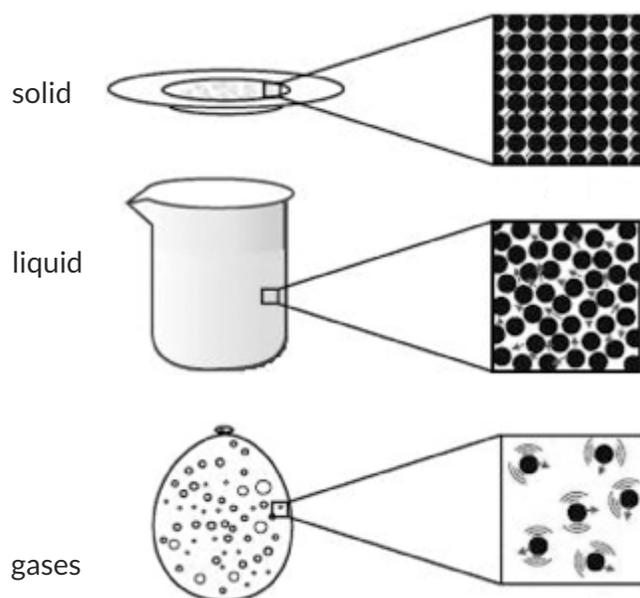
### Illustrations:

The diagrams or models used in textbooks can be misleading. For example, the expansion of solids when heated and the decrease in density when solids melt is greatly exaggerated in diagrams. On the other hand, the decrease in density when a liquid changes to gas is under-represented, and liquids are usually represented in a way that suggests they are readily compressible.

The number of molecules shown in most diagrams does not convey a clear idea of how many particles are being talked about. So the impression of 'bulk' properties arising out of the combined action of very large numbers of particles is absent.

Finally, the colour of a bulk material is shown by colouring the particles, conveying the impression that the particles are coloured. So a chlorine atom becomes green and a carbon atom is black! Water molecules are usually shown floating in a blue background, conveying the impression that water and its molecules are two independent things.

This illustration from a current class 9 NCERT science textbook is a good example of how misleading diagrams can be and how they can convey misconceived ideas. If the depiction is correct, the density of the solid would be at least twice that of the liquid form of the same substance, and the density of the liquid would be only around four times that of the same substance in the gaseous state. This is obviously not true of any known substance.



### Imprecise statements:

Teachers sometimes resort to shortcuts, and end up making inaccurate statements. For example, they may say water consists of hydrogen and oxygen. This is imprecise. Water consists of water molecules with no trace of any property whatsoever of hydrogen and oxygen. The water molecule is made up of two atoms of hydrogen and one atom of oxygen.

### Casual treatment:

The casual nature of instruction can also cause problems, leading students to give erroneous explanations of a given phenomenon since they are unable to distinguish between the conceptual inputs required for the explanation. For example, boiling is a high energy phenomenon in which water turns to steam. On the other hand, electrolysis of water occurs when a seemingly small amount of energy from a battery is passed through water. In such a situation students often erroneously conclude that water 'boils' to give hydrogen and oxygen (both gases) since they cannot judge which categories apply where.

### **Analogies:**

We often look for analogies to explain various phenomena. So do most students, often erroneously. For example, students may use ageing in humans as an analogy for rusting of iron. A child named Nirjuli grows up and ages – height, weight, shape all change – yet she remains Nirjuli to the end. Similarly, iron may rust but continues to be iron – because rusting is in the nature of iron, which continues unchanged within the dusty brown product. So, this wrong analogy indicates that students do not realise rust is not same as iron, but a new product.

### **Student responses:**

Students quickly learn to give the correct answers without really understanding a phenomenon. Teachers also tend to accept these expected answers because no adequate probe is made to check whether learning has taken place or not. For example, students can correctly associate the right technical term with the event or phenomenon but cannot give a coherent

account of the process. If shown a piece of ice kept at room temperature, they correctly say it is melting, but have no idea what melting means.

It isn't only students. Even adults, including teachers, face difficulties. In a small study, several teachers were shown the picture from the NCERT textbook and asked: "What is present in the space between the molecules in the case of gases?" Some responded, saying there is air between the gas molecules. Some felt there is an intermolecular force between the molecules. Only a few said there is nothing between the molecules.

Similarly, several teachers felt an atom of copper would be a better conductor of electricity and heat than an atom of mercury. Interestingly, many teachers felt one would be able to measure the temperature of an atom if provided with the right type of instruments. That means that some teachers even believe that the bulk properties of a substance - like temperature, conductivity, etc - are also properties of these atoms/molecules.

## **What students need to know**

If students are to internalise the concept of the particulate nature of matter, they need to appreciate how these ideas developed. They must also get some exposure to the following ideas/concrete experiences before they move on to the theoretical issues.

### **Chemical change vs physical change:**

How does one know that a chemical change has taken place and a new substance has been formed? Very often, there are some seemingly straightforward clues to recognise that a chemical change has taken place. But students need to perform experiments where they can distinguish between a chemical change and a physical change and understand the conditions

under which these changes take place. For this, they need to be able to perform simple tests to find out the properties of substances and how the properties of the starting materials and products are different.

### **Specific properties of substances:**

Students need to gain familiarity with simple tests that show different chemical substances have different properties, which can be tested and observed. They need to have some experience of distinguishing substances on the basis of their chemical properties. For example, metals may appear similar but they differ markedly in their reaction with acids and this can easily be studied.

**Different states of matter, their properties, change of state:**

Students often have no conception of what is happening at the sub-microscopic level during a change of state, and how the change of state can be brought about, even if they know the correct terms for the processes taking place. The energy exchange in changes of state may be more apparent in some cases but not in others. For example, the supply of energy during the process of boiling water is fairly obvious but isn't as easily apparent when ice melts. Or again, the same amount of energy is released in the reverse processes of condensation and freezing, but this is never stressed or understood.

Similarly, cooling caused by evaporation is never fully understood. In this particular case, one way to enhance understanding might be to observe changes more closely during different seasons. In colder climes it is folk wisdom that it gets warmer after it snows, and it gets colder when the snow melts. What are the situations that people living in warmer places can use? Understanding that evaporation of water is a cooling process isn't

simple because when evaporation takes place on a large scale, we often feel 'hotter' because the humidity makes us sweat more. Maybe condensation of water vapour could be studied in detail to appreciate the same process in reverse.

**Elements, compounds and mixtures, how they are different from each other, how we identify these categories:**

It is important to go into the twin questions of separation and purity here. Our classification of a substance as pure would depend on the techniques of separation available to us and the methods for testing the purity of a sample. Till isotopes were recognised, the mixture of Cl-35 and Cl-37 found in nature was taken to be 'pure' (which it still is for purposes of studying chemical changes!).

Some simple experiments that cover the above areas are given in the third part of this module. Students should first attempt to perform these and similar experiments to lay the groundwork for grappling with atomic theory and related abstract ideas, and doing the problem exercises contained in other sections of the module.

# Appendix 1

## The Cannizzaro method of calculating atomic weights

In 1858, Stanislao Cannizzaro applied Avogadro's hypothesis to select the correct weights for the atoms of the different elements. Here are his postulates:

- The atomic theory states that all atoms of any element have a definite weight.
- Since molecules such as the hydrogen molecule or the water molecule contain definite numbers of atoms, they must have definite weights, which we refer to as formula weights.
- These formula weights contain one atomic weight (or a whole number multiple of that atomic weight) for each element present.

Based on these postulates, he proposed a method to calculate atomic weights, following the steps given below:

- If all gases have an equal number of molecules in equal volumes, their densities will be proportional to their molecular weights, i.e.  $M \propto D$  or  $M = KD$ , where  $K$  is a constant,  $M$  is the molecular weight of the given gas, and  $D$  is the density of the given gas.
- If we know the molecular weight of a gas, we can calculate the constant  $K$  from its density. For example, hydrogen has a molecular weight of 2 and oxygen 32. Therefore:

Gas	Molecular weight	Density	K
Hydrogen	2	0.09	22.25
Oxygen	32	1.43	22.4

- To calculate the atomic weights of, let's say, carbon and chlorine, we have to find out the molecular weights of various gaseous compounds of carbon and chlorine from their densities:

Gaseous Compound	Density	Molecular weight (Density x K)
Methane	0.72	16
Ethane	1.34	29.9
Chloroethane	2.88	64.3
Choloroform	5.34	119.5
Carbon Tetrachloride	6.83	152.99

COMPOUND	WEIGHT PERCENTAGE			AMOUNT in ONE MOLE of the compound (in gram)			PROBABLE FORMULA
	CARBON	HYDROGEN	CHLORINE	CARBON	HYDROGEN	CHLORINE	
METHANE	74.8	25	-	12.0	4.03	-	CH <sub>4</sub>
ETHANE	79.8	20	-	23.9	6.04	-	C <sub>2</sub> H <sub>6</sub>
CHLOROETHANE	37.2	7.8	55	23.9	5.02	35.04	C <sub>2</sub> H <sub>5</sub> Cl
CHLOROFORM	10.05	0.85	89.1	12.2	1.01	106.2	CHCl <sub>3</sub>
CARBON TETRACHLORIDE	7.8	-	92.9	11.01	-	141	CCl <sub>4</sub>

- After calculating the molecular weights, we need to find the percentage weight of every element in each compound experimentally. The probable formula that can be derived from this information is given in the following table, which also gives the calculation method:
- Let us see how the above information is derived from the data. Step 4 gives 16 as the molecular weight of methane. The percentage of carbon in methane (column 2) is 74.8. That is, 100g of methane has 74.8g of carbon. Therefore, 16g of methane (one mole of methane) contains  $(74.8/100) \times 16 = 12$ g of carbon. The other values in the table have been calculated in a similar manner.
- We have calculated the amount of every element in one mole of each of the compounds. Next, we look at the minimum amount of an element present in these compounds. We can see that one mole of each compound has different amounts of carbon. The minimum amount of carbon in one mole of its compounds is 12g. From this, we take the atomic weight of carbon as 12 because we assume that these compounds contain at least one atom of carbon. If later studies give us compounds that contain 6g or 4g of carbon/mol, we will have to revise the atomic weight of carbon and all the formulas calculated in the above table.
- What would be the formulas of methane if the atomic weight of carbon was 4 instead of 12?

The formulas of compounds can be calculated from the atomic weights of the elements by reversing the process.

## Appendix 2

### More problems related to laws of chemical combination

1. In a set of experiments designed to verify the law of definite proportions, very pure tin metal was quantitatively combined with elemental bromine, forming tin tetrabromide. Using the data given below, confirm the law by calculating the percentage of tin in each sample of the tetrabromide:

Grams of tin reacted	Grams of tin bromide formed
2.8445	10.4914
3.0125	11.1086
4.5236	16.6752

2. Direct combination of zinc and sulphur yields zinc sulphide. In a number of experiments, the weights of reacting zinc and sulphur are as follows:

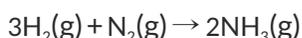
Grams of zinc reacted	Grams of sulphur reacted
5.776	2.831
10.428	5.114
2.453	1.204

Do these figures agree with the law of constant proportions?

3. Fluorine and oxygen combine to form a fluoride whose weight-percentage composition is 70.5% fluorine and 29.5% oxygen. Also, water decomposes to give 11.2% hydrogen and 88.8% oxygen by weight. Apply the law of reciprocal proportions to get the proportion in which fluorine and hydrogen will react.
4. Fluorine and oxygen combine to form a fluoride whose weight-percentage composition is 70.5% fluorine and 29.5% oxygen. These same two elements combine to produce a second fluoride whose weight-percentage composition is 54.2% fluorine and 45.8% oxygen. Show how these data confirm the law of multiple proportions. Suggest simple formulae for the two fluorides.
5. Determine the atomic weight of copper from the following facts: 63.5g of copper combines with 16.0g of oxygen to form a 1:1 oxide of copper (given that the atomic weight of oxygen is 16).
6. Magnesia refractories such as forsterite are composed of magnesia and silica.
  - a) Without consulting the periodic table of elements, can you figure out what the relative atomic weight of magnesium is if the Mg/O<sub>2</sub> combining weight ratio in magnesia (MgO) is 1.52:1.00? Compare your answer with the value given in the periodic table.
  - b) If the Si/O<sub>2</sub> combining weight ratio in silica (SiO<sub>2</sub>) is 0.878, what is the combining weight of silicon and what is its relative atomic weight?
7. Kaolinite refractories contain alumina (Al<sub>2</sub>O<sub>3</sub>). Given that the atomic weight of aluminium is 26.98, calculate the Al/O<sub>2</sub> ratio and the combining weight of aluminium.
8. The atomic weight of chromium is 52.01 and its combining weight with oxygen is 34.667. What is the chemical formula for the oxide?

9. The combining weight of molybdenum metal in one of its oxides is known to be  $O_2$ . The specific heat of molybdenum is known to be  $0.250\text{J/gK}$ . What is the atomic weight of molybdenum? (specific heat  $[\text{in J/gK}] \times \text{atomic weight} = \sim 25\text{J/mol.K}$ )

10. Hydrogen reacts with nitrogen to produce ammonia:



Determine how much ammonia would be produced if 100g of hydrogen is reacted completely with the required amount of nitrogen.

11. Sodium enters into two distinctly different chemical combinations with oxygen. Here are the percentage compositions of the products of these two reactions:

Sodium oxide:	74.2% sodium, 25.8% oxygen
Sodium peroxide:	59.0% sodium, 41.0% oxygen

How do these data demonstrate the law of multiple proportions?

12. Here are some data on the analysis of a set of compounds composed of only two elements, carbon and hydrogen (hydrocarbons). Show how these data can be used to demonstrate the law of multiple proportions:

Ethane	$\text{C}_2\text{H}_6$	79.89% carbon
Ethylene (ethene)	$\text{C}_2\text{H}_4$	85.63% carbon
Acetylene (ethyne)	$\text{C}_2\text{H}_2$	92.26% carbon

13. On the basis of the information below, determine the relative atomic weights for the atoms in each compound. Assume the formulas are correct and the atomic weight of hydrogen is 1.0.

HCl	2.74% hydrogen; 97.26% chlorine
NaCl	39.2% sodium; 60.7% chlorine
$\text{Na}_2\text{O}$	74.15% sodium; 25.85% oxygen
$\text{CO}_2$	27.3% carbon; 72.7% oxygen
$\text{CS}_2$	15.80% carbon; 84.20% sulphur
$\text{H}_2\text{S}$	5.9% hydrogen; 94.1% sulphur

14. It was found that the ratio of the weights of equal volumes of chlorine and oxygen was 2.22. What is the apparent molecular weight of chlorine, assuming oxygen to have an atomic weight of  $16.0\text{g/mol}$ ?

15. At room temperature and atmospheric pressure, a gram of oxygen occupies a volume of  $0.764$  litre, whereas a gram of an oxide of nitrogen under the same conditions occupies a volume of  $0.266$  litre. What is the formula weight of this oxide of nitrogen?

16. The specific heat of lead is  $0.13\text{J/gK}$ ; its combining weight in lead chloride has been found to be exactly  $103.605/35.453$  of chlorine.

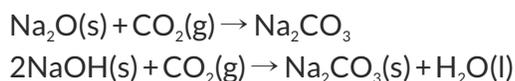
a) Using Dulong and Petit's law, determine the approximate atomic weight of lead.

b) Since the atomic weight must be an integral multiple of the combining weight, determine the correct atomic weight of lead.

c) What is the empirical formula for this particular chloride?

17. The specific heat of lead is 0.13J/gK. Its combining weight in a certain lead oxide is found to be exactly 138.133g. What is the empirical formula of this particular oxide?
18. The combining weight of elemental chromium in one of its common oxides was found to be 17.332g. Its specific heat is 0.510J/gK. What is the atomic weight of chromium?
19. The atomic weight of hydrogen is known to be exactly 1.008 atomic mass units. Nitrogen ( $N_2$ ) can be combined with hydrogen ( $H_2$ ) to produce ammonia ( $NH_3$ ). Data (obtained experimentally) shows the weight-percentage of nitrogen in ammonia is 82.25%. Calculate the atomic weight of nitrogen.
20. When a carefully weighed sample of an unknown metal M reacted completely with oxygen, it was found that the resulting oxide was exactly 10.30% oxygen by weight. If the empirical formula is known to be  $M_2O_3$ , what are the atomic weight and specific heat of the metal?
21. Calculate the weight of one chlorine atom and of one hydrogen atom. What is the ratio of the weight of 1000 chlorine atoms to the weight of 1000 hydrogen atoms? Compare this with the ratio of their respective atomic weights.
22. A mole of sodium atoms weighs 23.0g and a mole of chlorine atoms weighs 35.5g. What weight of sodium atoms must you buy in order to get the same number of atoms as there are in a mole of chlorine atoms?
23. A flask contains 28g each of carbon monoxide ( $CO$ ), ethylene ( $C_2H_4$ ) and nitrogen ( $N_2$ ). How many molecules are present in the flask?
24. State the percentage composition of each of the following:
  - a) Lithium in  $LiOH$
  - b) Carbon in  $SrCO_3$
  - c) Oxygen in  $Mn_2O_7$
  - d) Water in  $CuSO_4 \cdot 5H_2O$
  - e) Sulphur in  $H_2SO_4$

25. Alkali metal oxides and hydroxides have been successfully used to scavenge carbon dioxide ( $CO_2$ ) from the breathing space in closed human environments such as submersible vehicles and spacecraft. The reactions taking place can be represented by:



Calculate the theoretical removal of  $CO_2$  in grams of  $CO_2$  per kilogram of the reagent ( $NaOH$  or  $Na_2O$ ).

Write similar equations for  $Li_2O$  and  $LiOH$ , and determine whether on a weight basis  $LiOH$  is more effective than  $NaOH$  or not. Is  $LiOH$  more effective than  $Li_2O$ ?

26. Aluminium metal can be prepared by reducing aluminium chloride with sodium metal, producing sodium chloride at the same time. When a charge of 34.5g of sodium (atomic weight = 23.0g/mol) is used, 13.5g of aluminium (atomic weight = 27.0g/mol) is produced from 66.8g of aluminium chloride. Determine the simplest chemical equation that describes the process and agrees with these data.
27. A certain metallic element has an atomic weight of 24g/mol. A certain non-metallic element has an atomic weight of 80g/mol. When this metal and non-metal are combined chemically, they do so in a ratio of 1 atom to 2 atoms respectively.
- Determine the number of grams of the metal that would react with 5.00g of the non-metal.
  - How many grams of the product will be formed?
28. A flask contains 30g of nitrogen oxide (NO) and 30g of diimide ( $N_2H_2$ ). How many molecules are present in the flask?

## Part-3

# Some simple experiments to help students experience chemical change and the properties of substances

Students need to get a feel for chemistry by performing experiments. But they generally don't get enough opportunities to do experiments. It is important that they get some basic idea about the chemical properties of matter to lay the ground for understanding an abstract concept like atomic theory. For this they need to perform more qualitative as well as quantitative experiments.

This series of simple experiments gives them the opportunity to observe and study chemical changes and interactions between various substances. The first set of experiments helps them to assess the chemical nature of various substances and gain a qualitative understanding of why one substance is different from another. Next is a set of quantitative experiments that focuses on the concept of chemical equivalence, pointing out that equivalence cannot be deduced from the amounts (weights) of substances used in the reactions. Finally, there are a couple of experiments that will help students get an inkling of just how small the particles we are talking about are.

### Experiment 1:

#### Chemical properties - acids and bases

One chemical property that can be easily observed is acidic and alkaline natures of substances. Several indicators such as litmus and phenolphthalein can be used for the purpose. Litmus is available in strips while phenolphthalein is a powder that readily dissolves in water.

First, prepare a concentrated solution by dissolving phenolphthalein in alcohol or ether and then dilute it with water as and when required. Remember to use distilled water to prepare solutions for these experiments because substances dissolved in tap water may give confusing results.



*Testing solutions using different acid-base indicators*

Now collect various substances from the kitchen and test them one by one with the two indicators. Divide these substances into three groups on the basis of your observations: acidic, alkaline and neutral.

Follow this up by testing some chemicals, such as calcium carbonate, sodium carbonate, sodium bicarbonate, tartaric acid, citric acid, hydrochloric acid, etc.

You can also experiment with various flower colours to see if they can act as acid-base indicators. For this, mash the flower in water till the colour mixes fully or rub the petals on a piece of paper till the colour appears on the paper. Use the coloured paper the same way as litmus paper.

One thing needs to be kept in mind: most of the tests in this activity need an aqueous medium.

### Experiment 2: Titration

One thing becomes obvious after testing the acidic/basic property of various substances, that these are 'opposing' properties. Now look for an answer to the following question: What would happen if an acid is mixed with an alkali?

To find the answer, take two solutions – sodium bicarbonate and hydrochloric acid – and test them with litmus and phenolphthalein indicator to ascertain their nature. Next, titrate one solution with the other. For this, pour 20 drops of hydrochloric acid in a test tube and add 2 drops of phenolphthalein indicator. Then add the sodium bicarbonate solution drop by drop till the solution in the test tube becomes alkaline. Record the number of drops of sodium bicarbonate required to 'neutralise' 20 drops of the acid solution.

The same experiment can be done in a slightly different manner to get a feel for chemical equivalence (see experiment 14).

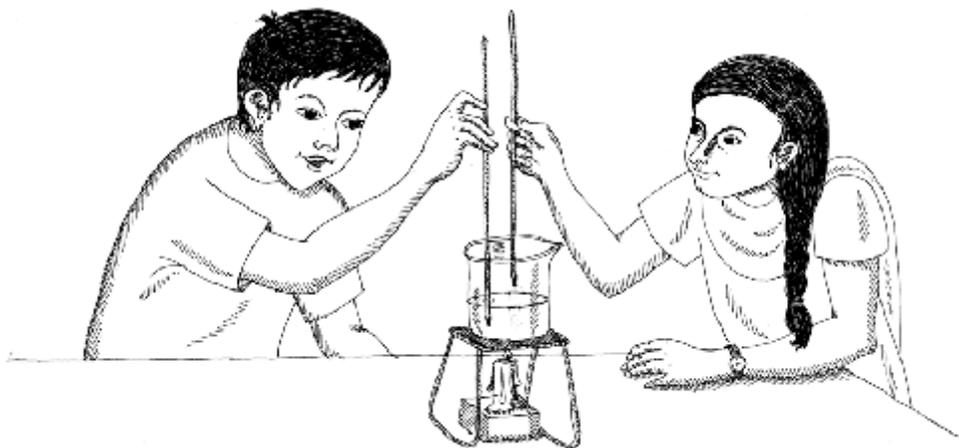


*Titration: How many drops of sodium bicarbonate solution is required to neutralise 20 drops of a solution of hydrochloric acid?*

### Experiment 3: Boiling point, change of state, evaporation and condensation

Record the boiling point of water, noting the temperature of the water as well as the water vapour. The temperature of the vapour can be read by holding the thermometer a little above the surface of the boiling liquid. What is important is that you should observe the change in temperature as the water is heated and also note that the temperature remains constant once the water starts boiling properly.

There is a misconception prevalent among adults as well as children – that the change of state occurs only at the boiling point. How do you address this? Do several experiments to get a hang of it. Also correlate your observations with your everyday experiences. Such as, answer the question: When water condenses on the outer surface of a glass containing ice, where does this water come from? Relate your answer to where water goes when clothes dry, and compare and contrast this process with the process of boiling. Is the amount of water that condenses different on days when clothes take a long time to dry compared to days when clothes dry quickly? In which case would the amount of water be less or more and why? Draw conclusions from your observations.

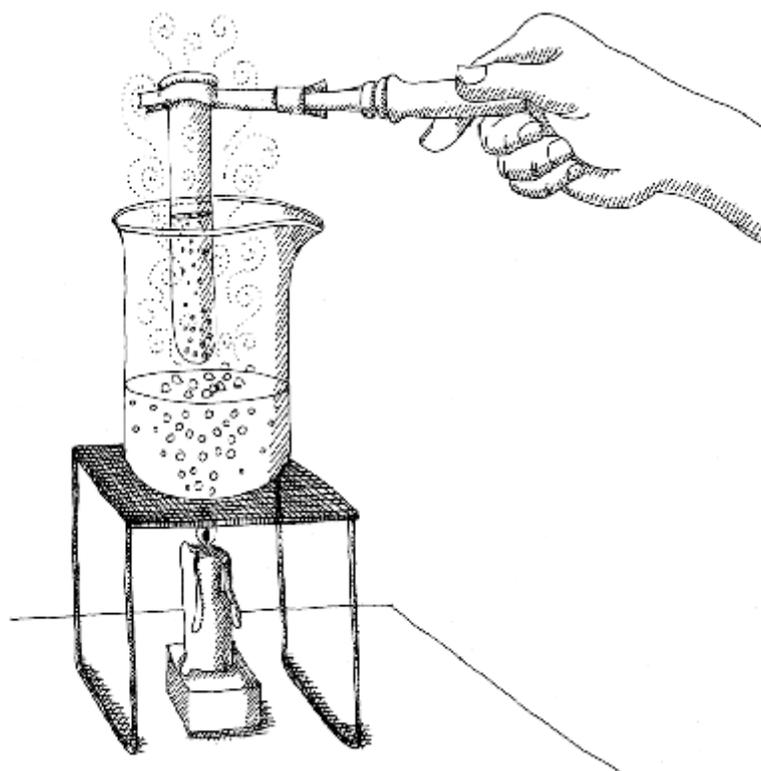


*Measuring the temperature of boiling water and the steam produced*

#### **Experiment 4: More on evaporation and condensation**

Fill a beaker about one-third with water, heat it till the water starts boiling and describe what happens. Next, fill cold water in a test tube and hold it over the mouth of the beaker in which water is boiling. What do you observe on the outside of the test tube? Repeat this step but this time fill the test tube with hot water. What do you observe now? Why is there a difference?

Students should study different types of reactions to understand, recognise and form a mental picture of chemical changes. Reactions such as rusting of iron can be studied both qualitatively (identifying the factors necessary for rusting) and quantitatively (estimating the amount of air used up when iron rusts in an enclosed space and calculating the percentage of oxygen in that air sample). The following chemical reactions are simple to organise and provide specific indications that a chemical change has taken place.



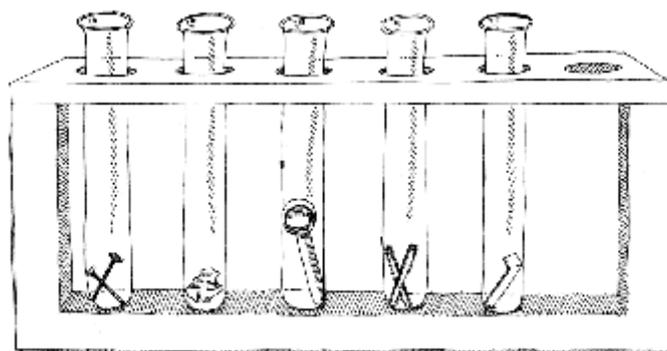
*A liquid evaporates when its temperature is increased and a gas condenses when it loses heat*

## Experiment 5: Some specific reactions

Make a dilute solution of copper sulphate in water and pour equal amounts of this solution in five test tubes. Put one of the following things in each test tube: an iron nail, a piece of aluminium foil, a match stick (without the masala), a plastic spoon, or a piece of paper.

Observe the test tubes after every five minutes and record the changes taking place in the different substances, including any change in colour.

This experiment brings out the idea that chemical reactions are specific. All substances don't react with all others, and even if more than one substance react with a given chemical, the reactions are different. It also gives one indication that a chemical change has taken place, viz., change of colour.



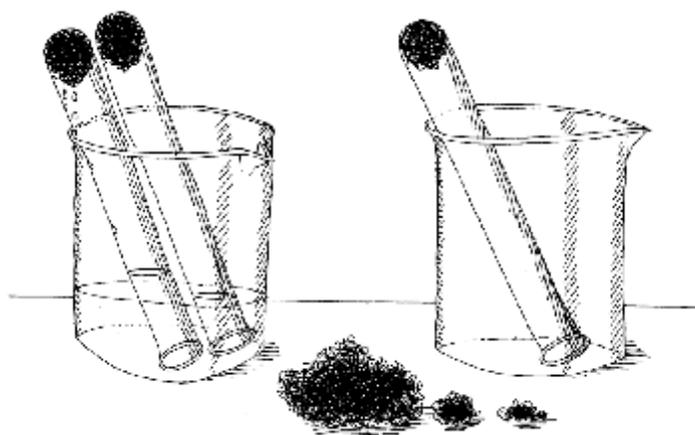
*Not all substances react with each other, chemical reactions are specific*

## Experiment 6: Rusting of iron

This is an interesting experiment because you can actually make measurements and draw conclusions. The results are most distinguishable if it is done during the summer when it is hot and dry. If this experiment is done during the wet season, the differences may not be noticeable. Take an iron scrubber (used for cleaning vessels in the kitchen), three test tubes and a beaker. Cut three small pieces of the scrubber, roll them into small balls and push a ball into each test tube till it gets stuck at the bottom.

Now fill the beaker one-fourth with water. Wet the ball in the first test tube with water and invert the test tube in the beaker containing water. Invert the second test tube in the beaker without wetting the ball. Keep the third test tube inverted in an empty and dry beaker. Note the water level in the test tubes inverted in the beaker of water.

After around two hours, observe whether the iron balls have rusted. Which samples show rusting? Is there a difference in the water levels of the two test tubes inverted in the beaker of water?



*Set-up for testing the factors affecting the rusting of iron*

Continue your observations as long as the water level keeps changing. Does it remain constant after some time? (This might take a few days depending on the ambient temperature.)

Explain your results, especially the relationship between rusting and change in the water level. Why does the water level change? Why does it stop changing after some time?

The next set of experiments involves preparing and studying the properties of gases such as hydrogen, oxygen and carbon dioxide. You can also prepare ammonia but this requires some extra precautions, so we have not included it.

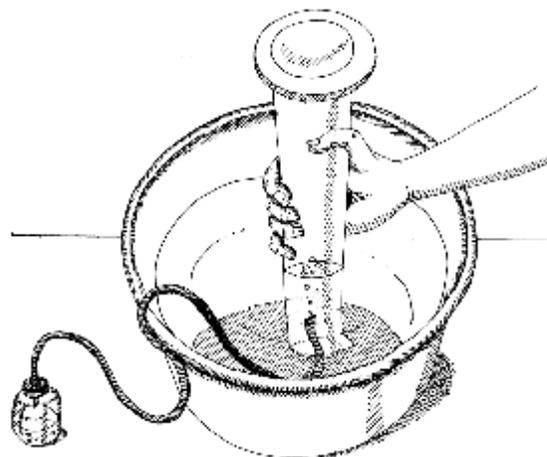
There is a problem in preparing and collecting a gas: it requires air tight apparatus, which is difficult to prepare. A simple alternative is described here: the materials are easily available, heating is not a problem and the gas can be easily collected.

You will need a 30mL injection bottle, a 3-4cm long empty ball pen refill, and a 30cm long piece of cycle valve-tube. Insert the refill through the rubber cap of the injection bottle. Attach the valve-tube to the exposed end of the refill. This set-up is air-tight and the reactions can be carried out in the injection bottle.

The gases formed can be collected by the downward displacement of water (see diagram). This set-up can also be used for preparing oxygen, the only added precaution being that the injection bottle should not be abruptly cooled after carrying out the reaction.

### Experiment 7: Preparing oxygen and testing its properties

Oxygen can be easily prepared by heating potassium permanganate. Put about half a spatula of potassium permanganate in an injection bottle. Then set up your apparatus so that you can collect the gas formed. Heat the injection bottle over a candle flame. Let the gas produced initially escape since it is mixed with air in the bottle. Then collect the gas in test tubes and conduct the following tests: litmus paper test (both red and blue); combustibility test (by inserting a lit incense stick into the test tube containing oxygen). (Note that though oxygen supports combustion, it does not burn itself.)



*An alternate set-up to collect and measure the gas being produced in a reaction*



*Testing for the presence of oxygen by bringing a lighted incense stick near the mouth of the test tube containing oxygen*

## **Experiment 8:**

### **Preparing carbon dioxide and testing its properties**

Carbon dioxide can be prepared by reacting marble chips with acid (preferably hydrochloric acid). Use the same set-up as above. You can study the properties of the gas collected by testing with litmus paper, passing it through freshly prepared lime water, reacting it with pink phenolphthalein solution, and observing its effect on combustion.

Carbon dioxide is heavier than air. You can demonstrate this by pouring the gas from one test tube into another and then testing for the presence of carbon dioxide in the second test tube.

We generally think that carbon dioxide does not support combustion, so an interesting experiment is to see its reaction with burning magnesium. For this, collect carbon dioxide in a gas jar, ignite a strip of magnesium ribbon and drop the ribbon in the gas jar. You can observe that the magnesium ribbon, which burns with a bright white light in the atmosphere, now burns with a yellow flame inside the gas jar. After the reaction is over, you will see black deposits inside the gas jar.

Magnesium forms a strong bond with oxygen, hence it can displace carbon from carbon dioxide. The carbon is deposited on the sides of the gas jar as soot while the magnesium oxide formed is seen as a white powder (which can be tested with litmus paper after dissolving in water).

## **Experiment 9:**

### **Preparing hydrogen and testing its properties**

Hydrogen can be prepared by reacting zinc with hydrochloric acid, using the same apparatus as described above. Put some zinc granules (two or three small pieces) in the injection bottle and add 4-5mL of hydrochloric acid. Collect the gas produced in the manner described above. Test it with litmus and check its combustibility by bringing a lighted candle near the mouth of the test tube containing the gas, whereupon it burns with a characteristic popping sound.

The fact that hydrogen burns but does not support combustion can be demonstrated through a simple experiment. Collect the gas in a conical flask and hold the flask upside down (the gas is lighter than air). Introduce a burning candle half way up the inverted flask. The flame is extinguished. Now withdraw the candle slowly. The flame magically reappears at the mouth of the flask. Repeat this a few times. If you observe closely you will realise that the gas is escaping and burning at the mouth of the flask with a pale blue flame.

When the candle is introduced inside the flask it does not burn in the presence of hydrogen. But when it is taken out, the wick again catches fire from the hydrogen burning at the mouth of the flask.

The preparation of gases affords an opportunity to observe that chemical reactions are processes which take place over a certain time period and are affected by various factors.

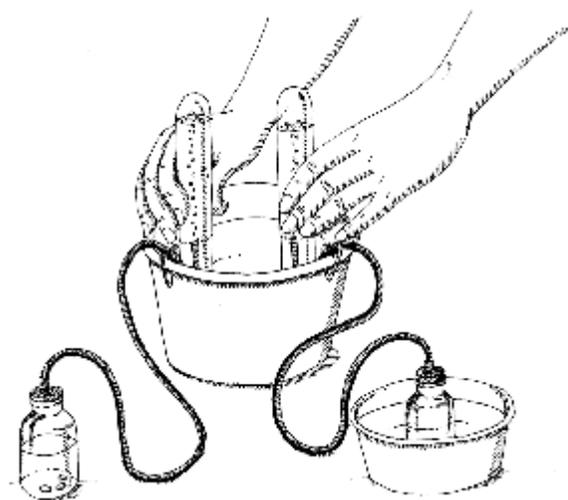
### **Experiment 10: Factors affecting the production of carbon dioxide**

The reaction of marble chips with hydrochloric acid can be used to study the factors that affect the rate of this reaction. You can try out different variations, such as the size of the marble chips, the concentration of the acid and the temperature at which the reaction is taking place.

You need to have two identical set-ups and vary one factor at a time. For example, take two samples containing an equal amount (by weight) of marble chips. Crush the chips in one sample to increase their surface area. Put the crushed and uncrushed samples in two injection bottles and pour equal amounts of acid into both bottles. Count and compare the number of bubbles formed in each bottle. Or compare the time it takes for each reaction to fill a test tube with gas.

Similarly, you can vary the concentration of acid poured into the two bottles (one more dilute than the other) containing an equal amount of marble chips and study the differences in the reactions.

To study the effect of temperature, put equal amounts of marble chips and acid in both bottles but keep the bottles at different temperatures: you can put one in hot water and the other in cold water.



*The rate of a reaction can be changed by changing the temperature*

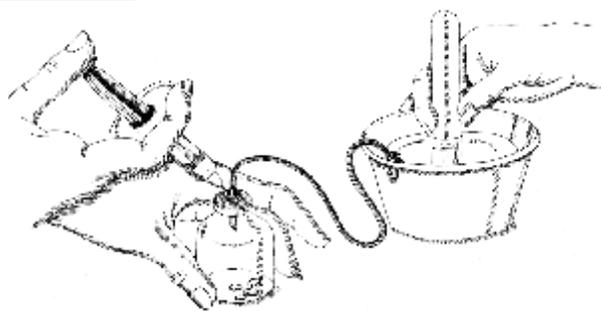
### **Experiment 11: Factors affecting the production of hydrogen**

You can compare the effect of the size of zinc pieces on the rate of reaction by putting zinc powder in one bottle and zinc granules in the other. The reaction will be faster with zinc powder.

Equivalence is an important concept in chemistry but it is important to remember that equal weights of two substances need not necessarily be chemically equivalent.

### Experiment 12: Chemical vs mass equivalence

You can study the reaction between a reactive metal and an acid (hydrochloric acid) to demonstrate that chemical equivalence is not the same as mass equivalence. Take equal weights (say 0.1g) of two metals (magnesium and zinc) and react them separately with the same amount of hydrochloric acid. Collect the gas produced in both cases and measure its volume. To make sure that the volume of the gas produced is measured accurately, the acid can be injected into the reaction bottle (injection bottle) as shown in the diagram.



*Set-up for preparing and collecting a gas.  
The acid can be added to the injection  
bottle using a syringe so that none of the  
gas produced escapes*

### Experiment 13: Chemical vs mass equivalence - titration

Take equal amounts of tartaric acid and sodium hydroxide. You can do this by putting two pellets of sodium hydroxide in one pan of a balance and then slowly adding tartaric acid to the other pan until the two balance. Now dissolve these substances in equal amounts of water (distilled if available). You can check whether equal amounts of these solutions would neutralise each other by actually doing the experiment.

While this is a good experiment to give you a feel of non-equivalence of equal amounts of different substances, you can calculate the amounts that are equivalent in terms of acidity/alkalinity. You know that you have dissolved equal amounts of acid and base in equal amounts of water. So each drop of the acid and base solutions contains equal amounts of acid and base respectively. If 20 drops of the acid solution is neutralised by, say, 30 drops of the alkali solution, you can infer that 1g of acid neutralises 1.5g of the base.



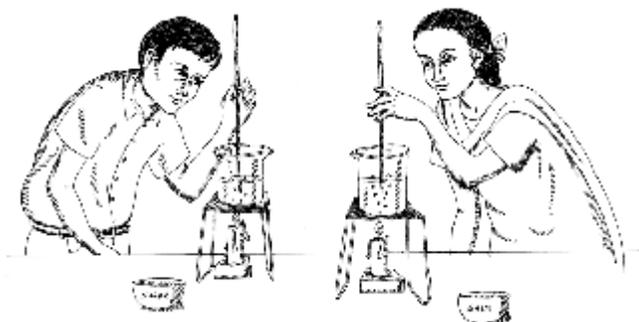
*Substances that weigh the same are not  
used up in the same manner  
in chemical reactions*

### Experiment 14: Chemical vs mass equivalence - Colligative properties and equivalence

Take around 100mL of water in a beaker and suspend a thermometer in it without its bulb touching the bottom or wall of the beaker. Heat the beaker over a candle. Note the change in temperature as the water heats. Also note that the temperature remains constant as long as the water is boiling. Record the temperature of both the water and the water vapour.

Next, take equal quantities of water (100mL) in two beakers. Add some salt to one beaker and an equal amount of sugar to the other. Heat both the

solutions and note the change in boiling point in both cases. The extent to which the boiling point is raised will differ. This is another indication that mass equivalence (roughly) is not the same as chemical equivalence. The elevation of the boiling point depends on the number of particles of the solute in the given volume of the solution.



*The boiling point of any liquid is affected by the addition of a solute to it*

It is important to convey an idea of how small the particles we are talking about are. Two activities can be done to demonstrate this. In one we see a large volume of water coloured by a tiny crystal of potassium permanganate – implying that the crystal breaks up into minute particles and spreads across the entire volume of the solution. In the other we calculate the thickness of an oil film formed on water, the assumption being that the layer formed is only one molecule thick.

### **Experiment 15:**

#### **Particle size - dissolving potassium permanganate crystals**

Dissolve a crystal of potassium permanganate in 10mL of water. Take 1mL of this solution and dilute it with 9mL of water. Is the new solution still coloured? This is the equivalent of dissolving the original crystal in 100mL of water. How much further can the solution be diluted before it becomes indistinguishable from ordinary water? Imagine how small the particles of potassium permanganate must be to spread across such a huge volume.

### **Experiment 16:**

#### **Molecule size - oil film on water**

You can estimate the size of a molecule in this activity by using the observation that oil spreads on water, the assumption being that the oil film makes a single molecule thick layer on the water surface. In order to find the thickness of this layer, all we need to know is the initial volume of the oil drop and the area of the film formed. The volume/surface area ratio gives us the thickness of the film, which is approximately the size of a molecule.

Since we need a very small volume of oil, dissolve 0.2mL of oil (any cooking oil or oleic acid) in 10mL of an organic solvent (say, hexane). You can easily calculate the volume of one drop of this solution. Pour some water in a large flat plate and allow it to become still. Sprinkle talcum powder on the surface. This helps to clearly demarcate the area of the oil film and this should be done just before you add the oil drop. Otherwise the water wets the talcum powder and stops it from spreading on the surface. Now use a syringe to gently add one drop of the oil solution to the water. The hexane (or organic solvent used) evaporates as soon as the film spreads out, leaving behind a circular oil film whose diameter can be measured. You can then calculate the approximate size of an oil molecule.



*Finding out the thickness of an oil film to estimate the size of a molecule*

## Acknowledgements:

Eklavya has tried out two different approaches to the particulate nature of matter, the first one was an experimental route which was developed by Dr. Pramod Upadhyay and Dr. Shashi Saxena and this was tried out while training HSTP resource teachers.

This module takes a historical approach, but nonetheless owes its inspiration to the earlier attempt. This approach has been tried out in three trainings and has further been tested with school and college students, and the feedback and comments from all these trials have gone into making this module more coherent and meaningful.

In addition, many members of our resource group have gone through the module at different stages and given various helpful suggestions which have been incorporated into it.

These include: Vijaya S. Varma, Amitabha Mukherjee, Pramod K. Srivastava, N. Panchapakesan, the late M. M. Kapoor, Patrick Dasgupta, Anand Fadnis, G. S. Holkar, Kamal Mahendroo, Arvind Sardana and Aamod Karkhanis, Bhas Bapat, Ankush Gupta, Sumit Tripathi and Laltu (Harjinder Singh). Also, present and past members of the Science team – Himanshu Srivastava, Shubhra Mishra and Reena Purohit – put in considerable work into getting diverse details right. Sonali Biswas took a keen interest in the subject matter in order to get the illustrations just so.

Rex D'Rozario worked on the text to fine-tune it and make it more readable. Sanat Mohanty went through the final text to check the content for the technical details. The final editing and layout was done by the Eklavya publications team. We shall make the usual caveat that any mistakes can be attributed to us.

Sushil Joshi

Uma Sudhir

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- Victor Meyer 47

## We dedicate this module to Rex

Rex did not just edit this module, he also oversaw most of Eklavya's publications while they took their baby steps. Likewise, he also encouraged all new people who joined to give their best the way he always did. He set an almost impossible standard of perfection, and we shall remember him as we try to live up to it - with affection, with respect, and with a never-diminishing sense of loss.





## High School Science Series

For many years now, Eklavya and its Academic Resource Group have been deliberating upon high school science curricula. Science is currently taught in schools as general science till class X, and the prescribed textbooks focus on introducing students to a large variety of topics in a cursory manner. We therefore felt that there was a strong need to develop resource materials for teachers and students in line with the philosophy of the Hoshangabad Science Teaching Programme (a pioneering educational initiative that spanned three decades, in over a thousand schools of some districts of Madhya Pradesh). Members of Eklavya, science teachers, scientists, educationists and others interested in education all put their heads together to develop a series of modules. These books are each the outcome of extensive collaborations, workshops, discussions, field trials and testing. They are designed to convey a broader understanding of some concepts and topics covered in school syllabi.



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