

The Principles of Chemistry



Dmitri Mendeleev · 1903

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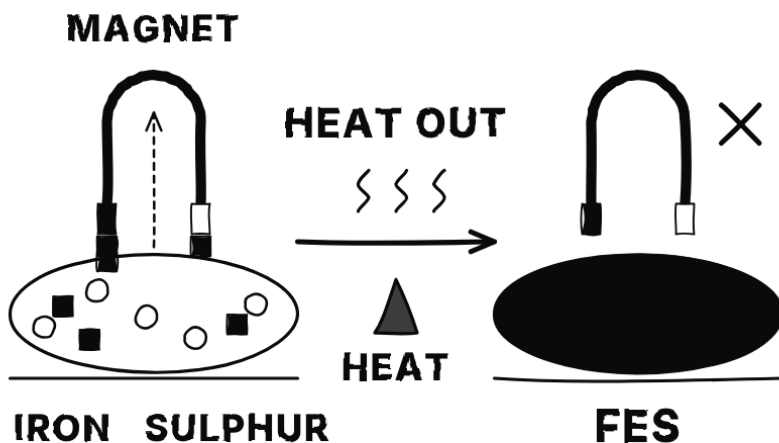
Introduction

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Having begun to develop rapidly from the time of Galileo (died 1642) and Newton (died 1727), the study of the outer world set chemistry apart as a special branch of natural philosophy, not only because of the growing number of observations and experiments concerned with the transformation of substances, but above all because, besides gravitation, cohesion, heat, light and electricity, it became necessary to recognise in all the smallest parts of every substance and body of nature special internal forces, which act plainly when some substances are transformed into others, but which under ordinary conditions are hidden, and therefore are not directly perceived and were long not acknowledged. The immediate subject of chemistry is the study of the homogeneous substances of which all the bodies of the world are composed, of their transformations into one another, and of the phenomena that accompany such transformations. All chemical changes, which are called reactions, take place only when the acting substances are in full and the closest contact, and they are determined by forces belonging to the smallest, invisible particles (molecules) of matter.



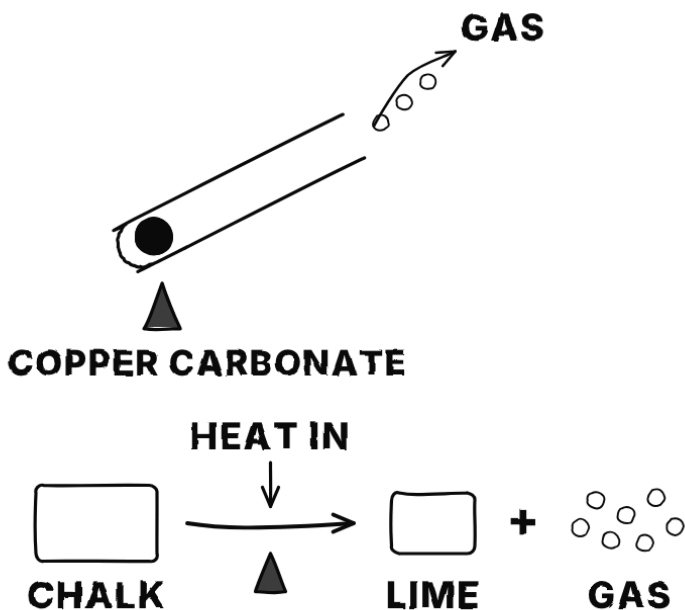
Iron and Sulphur Combine

Three principal kinds of chemical transformation must be distinguished:

1) Combination is a reaction in which one substance arises from two, or, in general, a smaller number of substances from a given number. Thus from iron and sulphur, when heated, a new substance arises: iron sulphide. In it the parts of the component substances cannot be seen, even under the strongest magnification. Before the reaction the iron can be drawn out of the mixture with a magnet, and the sulphur with oily liquids; in general they can be separated from each other mechanically as long as combination has not taken place, but after it both substances penetrate each other and can no longer be separated or told apart. Most often reactions of direct combination are

accompanied by the evolution of heat, and the ordinary cases of burning, which develop heat, consist in the combination of a combustible substance with a part (oxygen) of the air, whereby the gases and vapours contained in flame and smoke are formed.

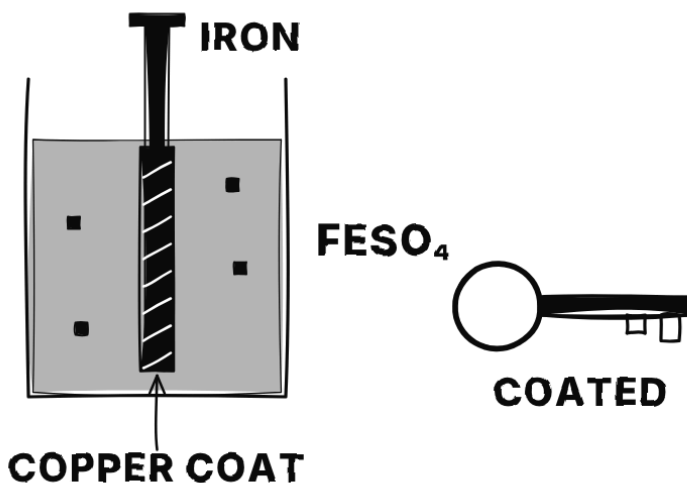
2) Reactions of decomposition are the cases opposite to combinations, that is, those in which one substance gives two, or, in general, a given number of substances gives a larger number. Thus when wood (as well as coal and many vegetable and animal substances) is strongly heated without access of air, a combustible gas, a watery liquid, resin or tar, and charcoal are obtained. In this way tar, illuminating gas and charcoal are prepared on a large scale in factories. Limestones, for example ordinary flagstone, chalk and marble, decompose when strongly heated, leaving lime and forming a particular gas called carbonic acid gas. A decomposition similar to this, but at a far lower temperature, one that thin glass can bear, takes place with the green copper carbonate that forms part of malachite. This example of decomposition will be described in more detail presently. If heat is evolved in ordinary reactions of combination, reactions of decomposition usually absorb heat.



Heat Splits One Into Several

3) The third kind of chemical reaction, when the number of acting substances equals the number of those produced, consists, as it were, of decomposition and combination together. If, for example, bodies A and B are given and from them bodies C and D arise, then, imagining that A decomposes into D and E, and that E, combining with B, gives C, we obtain a reaction in which two bodies were taken, A, or DE, and B, and two others were produced, C, or EB, and D. Such reactions may in general be called displacements, and in particular, when two substances give two new ones, the reaction is called substitution or double decomposition. Thus, if we take a solution in water of blue vitriol, that is, copper sulphate, and dip iron into it, copper is formed, or is set free, and the solution comes to contain iron (or green) vitriol, which differs from copper vitriol only in that iron has taken the place

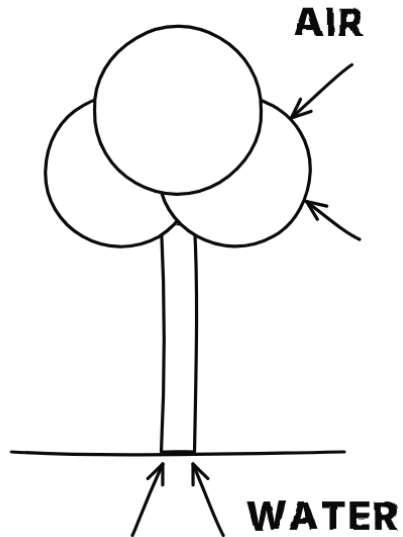
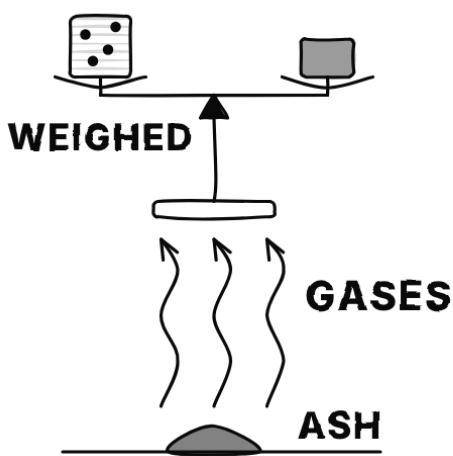
of copper in it. In a similar way iron can be coated with copper, and copper with silver, and such reactions are very often used in practice.



Iron Takes Copper's Place

Most of the chemical transformations that take place in nature and in factory processes are very complex, because they consist of many separate combinations, decompositions and substitutions taking place at the same time. In this natural complexity of chemical phenomena we must see the first reason why for a long time, for whole centuries, although people knew many chemical transformations and made use of them, they had no scientific chemical knowledge, that is, they did not study chemical changes, could not foresee them and could not control them at will. Another reason for the late development of chemical knowledge is the part played by gaseous substances,

especially air, in many reactions. A correct idea of the weight of air, and of gases in general as a particular elastic state of substances that spreads out in all directions, was obtained only in the sixteenth and seventeenth centuries, and only after that could the science of the transformation of substances be born. Until that time, without the idea of the invisible yet weighable gaseous and vaporous state of substances, no well-founded chemical knowledge of any kind could arise, because gases were left out between the acting bodies and those produced. Thus, under the impression of the phenomena we observe, one can easily form the notion that matter is, as it were, created and lost: whole masses of wood burn away, and only a small quantity of charcoal and ash remains of them; from a seed whose weight is quite insignificant a large tree grows little by little. In the one case matter apparently disappears, in the other it is created. This conclusion is reached because the formation or absorption of gases, invisible to the eye, is overlooked. When wood burns, it undergoes a chemical transformation into gaseous products, which go off as smoke. The substance of the wood does not disappear; through the chemical process it is only transformed into a gaseous one. Very simple experiments can confirm this. By collecting the smoke one can see that it contains gases quite different from air, gases that can support neither burning nor breathing. These gases can be weighed, and one then sees that their weight is greater than the weight of the wood taken. This increase in weight comes from the fact that in burning the component parts of the wood combine with a part of the air, just as iron increases in weight when it rusts. When gunpowder burns, its substance does not disappear, but is only transformed into powder gases and smoke.



ONLY THE FORM CHANGES

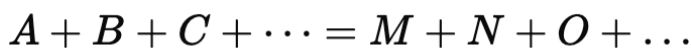
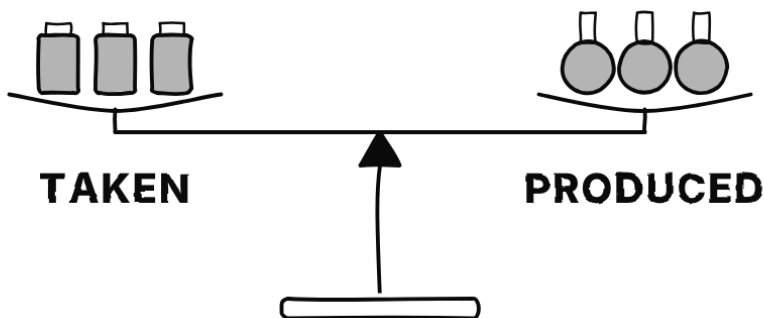
Matter Only Changes Form

In the same way, when a tree grows, the seed does not increase in mass out of itself; it grows only because it absorbs the gases of the air and, through its roots, absorbs from the earth water together with the substances dissolved in it. From these absorbed gases and liquids, by complex chemical processes directed by the forces acting in living organisms, are formed the saps of plants and the solid bodies that give them their shape. In a gas that does not contain the nourishing parts of the air, a plant does not grow, but dies. If moist objects dry and lose weight, if water evaporates, we know that it does not disappear, but returns again from the atmosphere as rain, dew and snow. If water soaks into the earth, it does not vanish there for ever either, but, having gathered somewhere under the ground, flows out of it as springs. Thus matter, undergoing various physical and chemical

transformations, only changes its place and form, but is neither lost nor created. It remains in the same quantity as it was before; in a word, matter is eternal for us. This simple and first chemical truth was hard to grasp by study, but as soon as it was made clear, it began to spread quickly, and now it seems to us as natural and simple as many truths established over the centuries. The eternity, or conservation, of the total quantity of matter was already suspected by some philosophers of ancient Greece and by scientists of the seventeenth century, for example Mariotte, but they did not trouble to express it clearly and to apply it to scientific ends. The experiments by which this simple law was grasped were made in the second half of the eighteenth century by the founder of modern chemistry, the French academician and farmer-general Lavoisier. Many of this scientist's investigations were made with the help of the balance, the only instrument by which one can judge the quantity of matter directly and exactly. Weighing every time all the substances and even the apparatus used for an experiment, and then weighing the substances obtained after the chemical transformations, Lavoisier found that the sum of the weights of the bodies produced was each time equal to the sum of the weights of the bodies taken, or, in other words: matter is neither created nor lost, or matter is eternal, or the mass (weight) of matter in nature is conserved, that is, remains constant. These last expressions, of course, contain a hypothesis, but by means of them a short phrase replaces the following long statement: in all our experiments and in all the phenomena of nature that have been studied, it has never once been possible to observe that the weight of the substances produced was greater or less (as far as the accuracy of weighing allows) than the weight of the bodies taken, and since weight is proportional to mass, or the quantity of matter, it follows from the above that it has never once been possible to observe the

disappearance of matter or the appearance of a new quantity of it. This law gives exactness to all chemical investigations, because on its basis an equation can be written for every reaction. If we denote by A, B, C and so on the weights of the substances taken, and by M, N, O and so on the weights of those produced, then:

SUM BEFORE = SUM AFTER



Lavoisier's Balance

Questions

1. Iron filings and sulphur are mixed, and later the mixture is heated. Which observation shows that a combination has taken place?

- a. The mixture has become darker in colour but still looks grainy
 - b. A magnet can no longer draw the iron out, and no part of either can be seen even under magnification
 - c. The sulphur can still be washed out with an oily liquid
 - d. The mixture now weighs less than the iron and sulphur did
2. Why did people for so long believe that matter is destroyed in burning and created in a growing tree?
- a. Because they overlooked the invisible gases that are formed or absorbed
 - b. Because burning really does destroy a small part of the wood
 - c. Because they had no way of making fire hot enough
 - d. Because trees grow only from the water in the soil
3. The gases collected from burning wood weigh more than the wood itself. Where does the extra weight come from?
- a. From the heat of the flame, which has weight
 - b. From the ash, which is heavier than it looks
 - c. From a part of the air that combines with the parts of the wood
 - d. From water that the wood soaked up earlier

Answers

1. **b)** Before the reaction the iron and sulphur can be separated mechanically; after combination they penetrate each other and can no longer be separated or told apart.
2. **a)** The conclusion that matter vanishes or appears is reached because the formation or absorption of gases, invisible to the eye, is overlooked.

3. c) In burning, the component parts of the wood combine with a part of the air, just as iron grows heavier when it rusts.

Practice

1. In the book's letters, bodies A and B give bodies C and D, where A is made of D and E, and C is made of E and B. Explain in your own words why this third kind of reaction can be called a decomposition and a combination taking place together.

Hint: Follow the part E: what does it leave, and what does it join?

Answer: A, which is D joined with E, comes apart into D and E: that is a decomposition. Then E joins B to give C: that is a combination. Two bodies went in and two came out, and the only change is that E has moved from D to B.

2. A wet cloth hung up to dry becomes lighter. Does this go against the law that matter is neither created nor lost? Explain.

Hint: Ask where the water from the cloth has gone, and whether it could be weighed there.

Answer: No. The water has not disappeared; it has evaporated into the air, an invisible state that still has weight, and it returns from the atmosphere as rain, dew and snow. The cloth is lighter only because part of the matter has changed its place and form.

3. Lavoisier weighed not only the substances but also the vessels and apparatus, before and after each experiment. Why was it important to weigh everything, and what did he find?

Hint: Think of the gases that can be taken up or given off unseen during a reaction.

Answer: Gases and other parts can pass unseen into or out of what is being studied, so only by weighing everything taken and everything

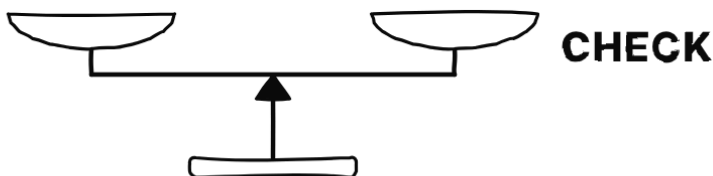
obtained can nothing be left out. He found that the sum of the weights of the bodies produced was each time equal to the sum of the weights of the bodies taken.

Introduction

$$A + B + C + \dots = M + N + O + \dots$$

$$A + B + C = M + N + ?$$

$$O = A + B + C - M - N$$

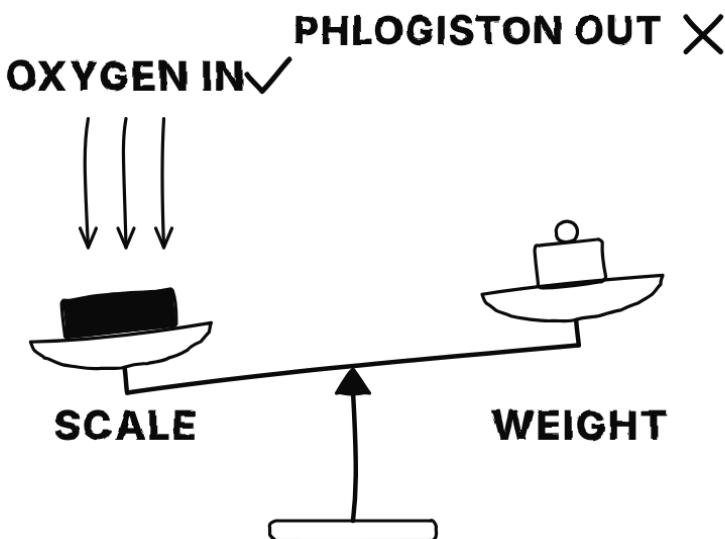


Finding the Unknown Weight

Therefore, if the weight of one of the acting or produced substances is unknown, this unknown weight can be found from the equation. By applying the law of the eternity of matter and by weighing, the chemist can always make sure that not one of the acting and produced bodies is overlooked. Having made such an omission, the investigator will notice it at once, because then the sum of the weights of the substances taken will not be equal to the sum of the weights of those

produced. On beginning the study of chemistry, one must become fully at home with the simple truth that this law expresses. We shall therefore give a few examples that make clear how the law of the eternity of matter is applied.

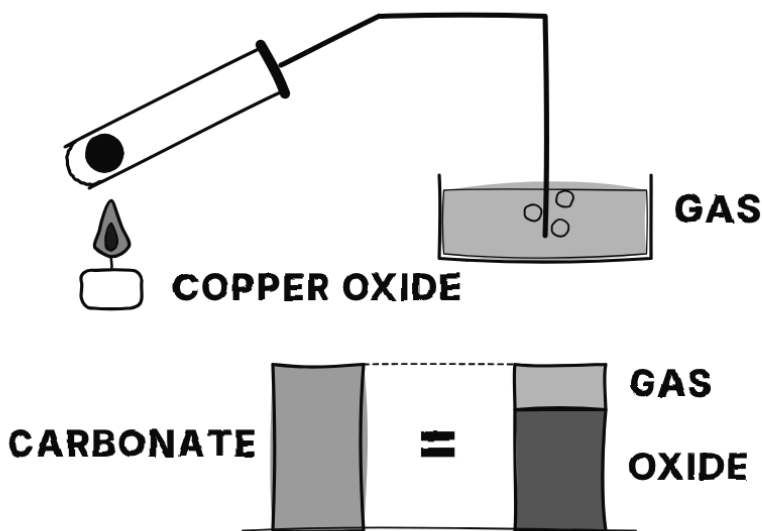
1) Everyone knows that iron rusts in moist air, and that when it is strongly heated in air it becomes covered with scale (an oxide), which, like rust, is an earthy substance resembling the iron ores that are found in the earth and serve for the extraction of iron. By weighing the iron before and after the formation of scale or rust, one can convince oneself that the weight of the metal increases in the process. It is easy to convince oneself also that this increase in weight comes, as Lavoisier showed, at the expense of that part of the air which is called oxygen and which serves for burning. Indeed, in a vacuum and in gases that do not contain the oxygen of the air, for example in hydrogen and nitrogen, neither rusting nor the formation of scale takes place. If no weighing were done, one could entirely overlook the part played by the oxygen of the air when iron passes into the earthy substances corresponding to it; and before Lavoisier this was overlooked, which is why phenomena like the one described were not understood. With the help of the law of the eternity of matter it is evident from the gain in weight that scale is more complex than iron, and that its formation is a reaction of combination. This chemical transformation could be regarded quite wrongly, for example by considering scale a simpler body than iron, and explaining the formation of scale by the removal of something from the iron. That is in fact how it was regarded before Lavoisier: iron was considered to contain a special unknown substance, called phlogiston, and scale to be deprived of this imaginary substance.



Scale Makes Iron Heavier

2) The green powder of copper carbonate sold in shops, as well as the well-known green stone called malachite, which is used for ornament and (as an ore) for obtaining copper, turn when strongly heated into a black substance called copper oxide. The same substance is formed when metallic copper is strongly heated in air, that is, it is the scale, or oxide, of copper. The weight of the black copper oxide that remains is less than the weight of the copper carbonate taken, and therefore we conclude that the reaction taking place is a decomposition, and that in it something is given off from the green copper carbonate taken. Indeed, if the mouth of the vessel in which the heating is done is closed with a tight cork, a gas delivery tube is passed through the cork, and its end is dipped in water, one can see that when the copper carbonate is heated a gas is formed, which comes out through the

delivery tube and through the water in bubbles. This gas is easy to collect, as will be explained further on, and one can then convince oneself that it differs quite clearly from air; for example, a burning splinter goes out in it, as if dipped in water. If weighing had not convinced us that a substance is given off, it would have been easy to overlook the formation of the gas, because it is transparent and colourless, like air. The carbonic acid gas given off can be weighed, and one can convince oneself that the sum of the weights of the black copper oxide and the carbonic acid gas is equal to the weight of the copper carbonate taken.

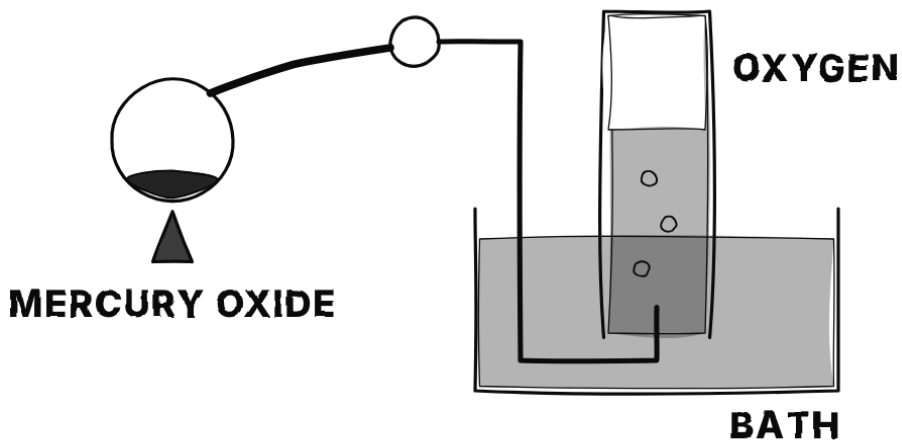


Copper Carbonate Gives Off a Gas

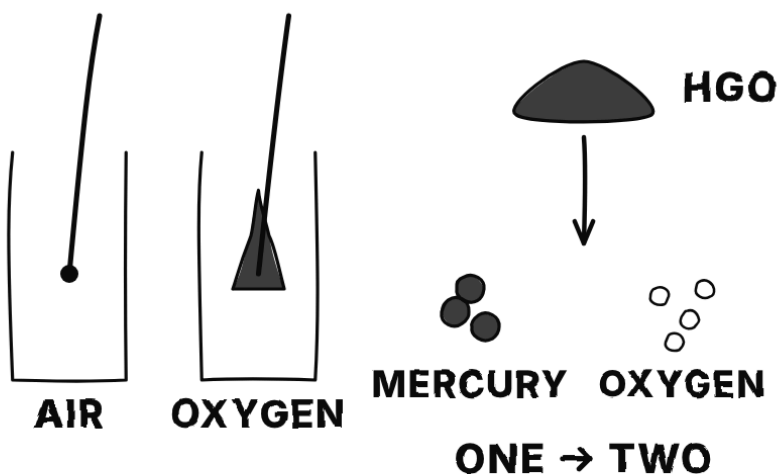
3) In a similar way, but with somewhat stronger heating and more slowly, red mercury oxide decomposes, forming a particular gas,

oxygen; red mercury oxide is formed as the scale of mercury when mercury is heated in air. For this a glass retort with mercury oxide is taken; the neck of the retort is fitted by means of a tight cork into one opening of a small glass bulb, and into its other opening a gas delivery tube, bent downwards, is fitted through a tight cork, as shown in the figure given here. The open end of the delivery tube is dipped into a vessel of water called the bath. If gases begin to be given off in the retort, they will have no other way out than through the delivery tube and the water of the bath, and so the giving off of gas will be visible as bubbles. When the retort with the mercury oxide is strongly heated, first air comes out, expanding from the heat, and then a particular gas called oxygen. The gas given off is easy to collect. For this a vessel is taken (usually a cylinder, as seen in our figure); it is filled with water to the very top, and, its mouth being stopped, it is turned upside down and the closed mouth is lowered into the water. Then the stopped mouth of the cylinder is opened. The cylinder will remain filled with water, that is, the water in it will stand higher than in the surrounding vessel, which depends on the pressure of the air on the water. The open lower mouth of such a cylinder is placed (under water) over the end of the delivery tube, and the bubbles of the gas coming out will pass into the cylinder. In this way gases can be collected. When enough gas has gathered in the cylinder, one can show clearly that it is not air, but another, particular gas, distinguished by its ability to support burning strongly. To see this, let us close the mouth of the cylinder under water, take the cylinder out, turn it mouth upwards, and lower a smouldering splinter into it. It is known that a smouldering splinter goes out by itself in air, but in the gas that is given off from red mercury oxide it bursts brightly and strongly into flame, which shows that this gas is able to support burning strongly and makes it possible to tell this gas from air. When red mercury

oxide is strongly heated, besides the formation of oxygen, one notices the appearance of metallic mercury, which turns into vapour in the heat and settles on the cold parts of the retort (and in the bulb fixed between the retort and the delivery tube) as a mirror-like layer or as droplets. Thus from red mercury oxide two bodies are obtained when it is strongly heated: mercury and oxygen. Here two new bodies arose from one, that is, a decomposition took place. Before the time of Lavoisier people already knew how to collect and study gases, but only he showed their true part in the course of many chemical transformations, which before him were either understood wrongly (as will be explained further on) or not explained at all, but only observed in their visible appearances. For the history of chemistry in Lavoisier's time it is precisely the experiment with red mercury oxide that has special importance, because the oxygen gas given off here is contained in the air and plays an enormous part in nature, especially in the breathing of animals, in the burning of bodies in air, and in the formation from metals of rusts and scales (calxes, as they were called at that time), that is, of earthy substances resembling the ores from which metals are extracted.



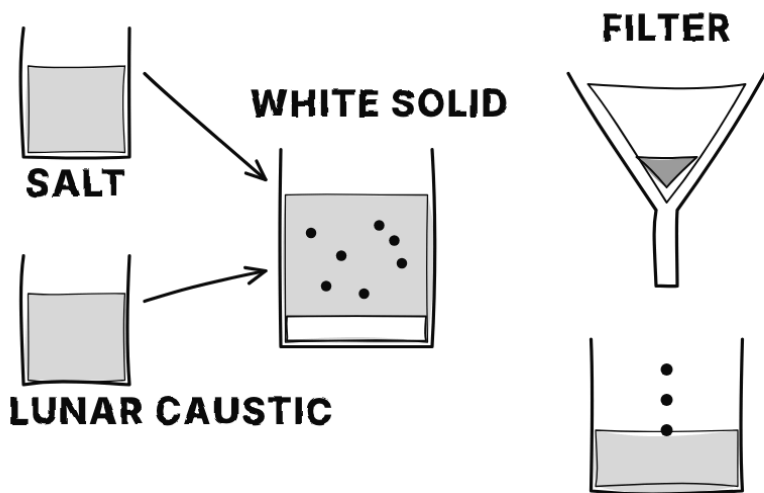
Collecting the Gas Under Water



Oxygen and Mercury

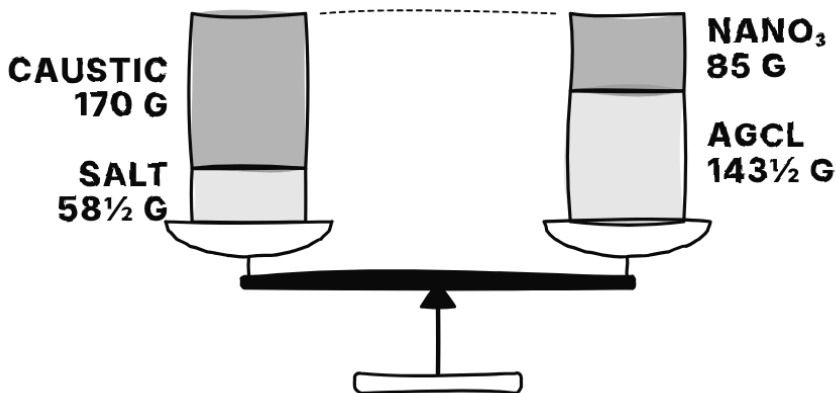
4) To show by one more experiment an example of chemical transformations and the applicability of the law of conservation of matter, let us take common salt and lunar caustic, with which, as is known, wounds are cauterised. Both these substances dissolve in water. Let us take clear solutions of each of these substances and mix them together. On this mixing we shall at once notice the formation of a solid white substance, which settles to the bottom of the vessel and is unable to dissolve in water. This substance that has separated out is easy to separate from the solution by straining. For this a glass funnel is taken, and in it is placed a circle of unsized paper, folded crosswise and opened out in the funnel so that a paper inner surface, or paper cone, is obtained in it, into which the cloudy liquid obtained by mixing the solutions of lunar caustic and common salt is poured.

Then the clear solution will pass through the paper (the strainer, or filter), and the powder that was suspended in the liquid will remain on the paper. It can be dried, and it turns out to be a quite different substance from those taken. This is already seen from the fact that it does not dissolve in water. By evaporating the liquid that has passed through the filter, we shall notice that it contains a new body, different both from common salt and from lunar caustic, but, like them, soluble in water. Thus here two substances soluble in water were taken, lunar caustic and common salt, and by substitution two new ones arose, one insoluble in water and the other remaining in solution. The water taken served only to bring the acting substances into a liquid and easily mobile state. If the lunar caustic and the salt are dried and weighed, and if about $58\frac{1}{2}$ grams of salt and 170 grams of lunar caustic are taken, then $143\frac{1}{2}$ grams of insoluble silver chloride and 85 grams of soluble sodium nitrate will be obtained. The sum of the weights of the acting and of the produced bodies will turn out the same and equal to $228\frac{1}{2}$ grams, as it should be by the law of the eternity of matter.



Mixing and Filtering

$$58\frac{1}{2} + 170 = 143\frac{1}{2} + 85 = 228\frac{1}{2}$$



228½ Grams Before and After

Questions

1. Iron heated in air becomes covered with scale and grows heavier. What does this gain in weight show?
 - a. That scale is iron combined with something from the air, a combination
 - b. That scale is iron which has lost its phlogiston
 - c. That heating makes every metal heavier, even in a vacuum
 - d. That scale is a simpler body than iron

2. Green copper carbonate, strongly heated, leaves black copper oxide that weighs less. Why is the gas it gives off so easy to overlook without a balance?
 - a. Because it is given off only very slowly
 - b. Because it dissolves completely in the water of the bath
 - c. Because it is transparent and colourless, like air
3. How can the gas from red mercury oxide be told from air?
 - a. It puts out a burning splinter, as if the splinter were dipped in water
 - b. A smouldering splinter bursts brightly into flame in it
 - c. It turns into mercury droplets on the cold glass
 - d. It makes the water in the cylinder rise
4. In the experiment with common salt and lunar caustic, what part does the water play?
 - a. It is one of the substances that reacts and is used up
 - b. It becomes the insoluble white powder
 - c. It adds its weight to the products
 - d. It only brings the acting substances into a liquid, easily mobile state

Answers

1. a) By the law of the eternity of matter, the gain in weight shows that scale is more complex than iron and that its formation is a reaction of combination, with the oxygen of the air.
2. c) If weighing had not shown that a substance is given off, the gas would have been easy to overlook, because it is transparent and colourless, like air.

3. **b)** A smouldering splinter goes out by itself in air, but in the gas from red mercury oxide it bursts brightly and strongly into flame.
4. **d)** The water taken served only to bring the acting substances into a liquid and easily mobile state.

Worked examples

Salt and lunar caustic on the balance About $58\frac{1}{2}$ grams of dry common salt and 170 grams of dry lunar caustic are made to react in water, giving $143\frac{1}{2}$ grams of insoluble silver chloride and 85 grams of soluble sodium nitrate. Show that the law of the eternity of matter holds.

The acting bodies are the salt and the lunar caustic; their weights together are $58\frac{1}{2} + 170 = 228\frac{1}{2}$ grams.

The produced bodies are the silver chloride and the sodium nitrate; their weights together are $143\frac{1}{2} + 85 = 228\frac{1}{2}$ grams.

The water is left out on both sides, because it served only to make the substances liquid and mobile.

The two sums are equal, as the equation $A + B = M + N$ requires.

Answer: Both sums are $228\frac{1}{2}$ grams, so nothing was created or lost.

Practice

1. Using the same experiment, suppose you weighed the $58\frac{1}{2}$ grams of salt, the 170 grams of lunar caustic and the $143\frac{1}{2}$ grams of silver chloride on the filter, but lost the liquid that passed through. How much sodium nitrate must it have contained?

Hint: Write $A + B = M + N$ and leave N, the sodium nitrate, as the unknown.

Answer: 85 grams. The acting bodies weigh $58\frac{1}{2} + 170 = 228\frac{1}{2}$ grams, so the produced bodies must weigh the same, and $228\frac{1}{2} - 143\frac{1}{2} = 85$

grams.

2. Before Lavoisier, scale was explained by saying that iron loses phlogiston when it turns into scale. Explain how weighing shows this explanation runs the wrong way.

Hint: If something is removed from the iron, what should happen to its weight?

Answer: If scale were iron with something removed, it should weigh less than the iron. But weighing shows the iron gains weight when it forms scale, and the scale does not form without the oxygen of the air. So something has been added, not removed: scale is iron combined with oxygen, a more complex body than iron.

3. Red mercury oxide, strongly heated, gives mercury and oxygen. Explain why this is a decomposition, and why the experiment mattered so much in Lavoisier's time.

Hint: Count the bodies before and after; then think where else the same gas is found.

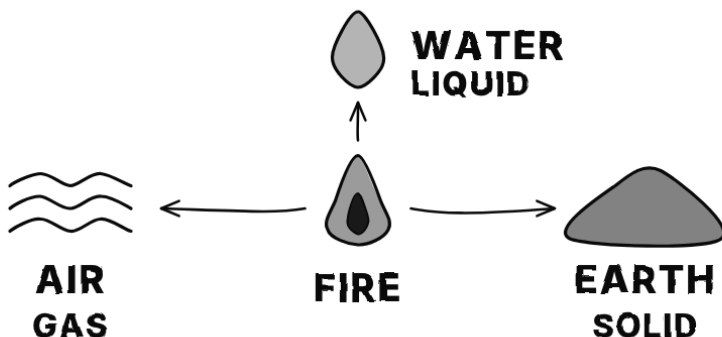
Answer: One body gave two new ones, so it is a decomposition. It mattered because the oxygen given off is the same gas contained in the air, which plays the great part in breathing, in burning, and in the formation of rusts and scales from metals.

Introduction

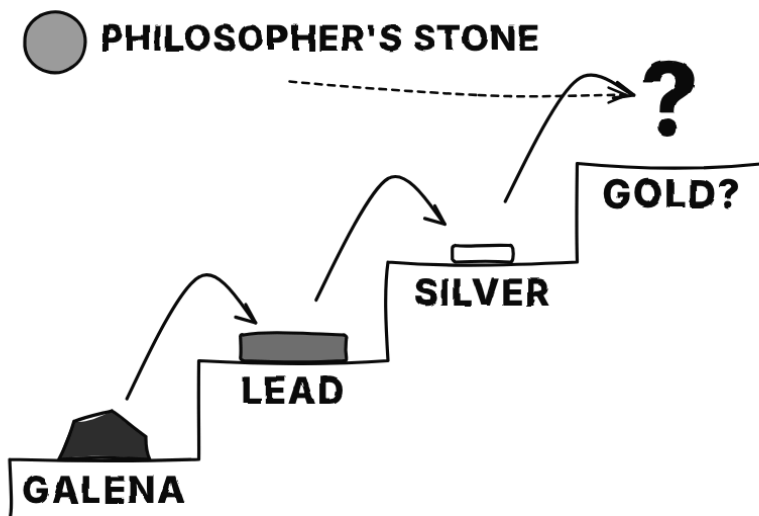
Once the law stated above is known, a question involuntarily arises: is there a limit to the diverse chemical transformations, or are they limitless, that is, can an equal quantity of any other substance be obtained from a given substance? In other words, is there an eternal, never-ending transformation of one kind of matter into all others, or is the circle of these transformations limited? This is the second most essential question of chemistry, the question of the quality of matter, a question evidently more complex than the question of quantity. A simple look at things cannot decide it. Indeed, seeing how the various substances of plants are formed from the air and the elements of the soil, how iron is turned into paints, for example into ink, Prussian blue and the like, one may think that there is no end to the qualitative changes of substances. On the other hand, everyday experience has led to the awareness that a nourishing substance cannot be made from stone, nor gold from copper, and so on. Therefore a definite answer must be awaited from study. This question was answered differently at different times. The opinion once most widespread in this respect held that everything visible consists of four elements: air, water, earth and fire. It has its origin as far back as Asia; from there it passed to the Greeks, and it was set out with particular completeness by Empedocles, who lived 460 years before Christ. This notion was not a conclusion from exact investigations, but was based, apparently, on distinguishing gaseous bodies (like air), liquid ones (like water) and solid ones (like earth), and on recognising their changes brought about by fire, that is, by heat. Arab scholars began to approach the solution of the question posed above by way of experiment. Through

Spain they brought into Europe a love of investigating questions of this kind, and from that time there appear many adepts of this science, which was considered mysterious and was called alchemy. The alchemists, not yet having a single strict law as a starting point for their investigations, answered the question of the transformations of substances in very different ways. Their great merit was that they made a multitude of experiments and discovered many new transformations, and everyone knows how some of them answered the fundamental question of chemistry.

LIMITED OR ENDLESS?



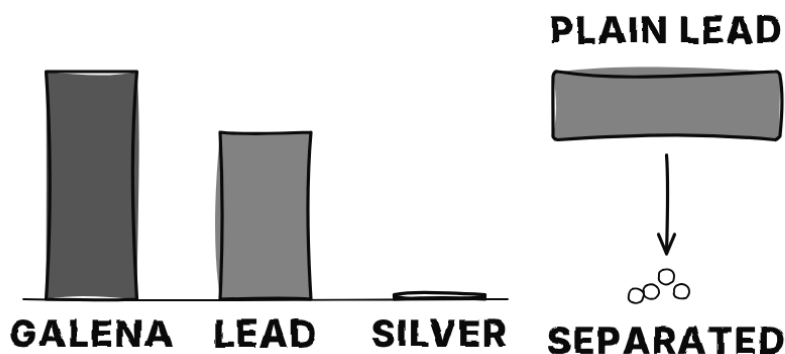
The Four Old Elements



The Alchemists' Ladder

Their view may be expressed as the recognition of an endless transformation of matter, because they searched for the philosopher's stone, able to turn everything into gold and diamonds and able to make an old body young again. This hypothesis was later rejected very sharply, but one must not think that the opinion of the alchemists sprang only from their imagination. The first chemical experiments could lead to such an opinion. They took, for example, a shining metallic stone called galena, and obtained lead from it. They saw that from one metallic body, unfit for use, another metallic substance is obtained, more ductile and valuable, which is used in practice. Further, they took this lead and obtained from it silver, more valuable still. From this they could conclude that by a whole series of transformations metals could be ennobled, that is, ever more precious

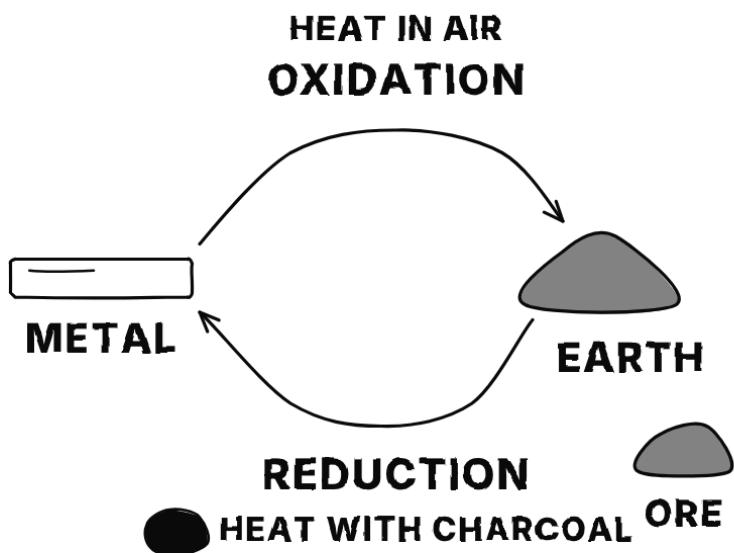
ones could be obtained from them. Having obtained silver from lead, they strove only to obtain gold from it. The incompleteness of their investigation is defined by the fact that they rarely weighed and in general paid little attention to quantities, while qualitative judgements are very often subjective and conventional. Had they weighed, they would have learned that the weight of the lead is much less than the weight of the galena, and that the weight of the silver is insignificant compared with the weight of the lead used. Had they studied the obtaining of silver from lead in more detail (and even now the main mass of silver is extracted from natural lead), they would have been convinced that lead does not turn into silver, but only contains a certain share of it, and that, once this has been separated, it can no longer give silver by any operations. The silver they extracted from lead was in the lead, and was not obtained through a chemical change of the lead. Today this is well known from experience, but a first view of a subject may quite naturally be mistaken. The path the alchemists followed in their study can never lead to complete success, because they did not set themselves simple and clear questions, by answering which they could have gone further. That is why they did not succeed in discovering a single exact law, but the alchemists left chemistry a legacy of many new experimental data.



What the Balance Would Have Shown

They studied especially many of the transformations proper to metals, and for that reason chemistry long concentrated on the study of metallic substances. In studying numerous chemical phenomena, the alchemists often made use of two chemical transformations, one kind of which is now called reduction and the other oxidation. The rusting of metals, and in general their passage from the metallic state into an earthy one, is called oxidation; and the reverse obtaining of a metal from an earthy substance is called reduction. A great many metals are oxidised merely by strong heating in air and are reduced again by strong heating with charcoal, for example iron, lead and tin. Many such oxidised metals are found in the earth. This is one of the kinds of metallic ores. From such ores, as from rust or scale, metals are obtained by strong heating with charcoal, for example tin, iron and

copper. These transformations were studied by the alchemists. Thus two transformations were known: the oxidation of metals and the reduction of the oxides obtained back into metals. The explanation of these two chemical phenomena gave occasion for the discovery of the most important chemical laws. The first hypothesis to explain them was given by Becher, and especially by Stahl, physician to the King of Prussia, in the *Fundamenta chemiae* of 1723. In his opinion, all bodies consist of a weightless fiery substance called phlogiston (*materia aut principium ignis non ipse ignis*), and of another element having particular properties for each substance. The more capable a body is of oxidation or burning, the more phlogiston was supposed to be in it, and in charcoal its content was considered very great. In oxidation and burning phlogiston is given off, and in reduction it is absorbed, or enters into combination. Charcoal reduces earthy substances precisely because it is rich in phlogiston: it gives them part of its phlogiston. Thus Stahl supposed that metals are complex bodies, consisting of phlogiston and an earthy substance, or oxide. Stahl's hypothesis is distinguished by very great simplicity, and partly for that reason it found a great many admirers.



Oxidation and Reduction

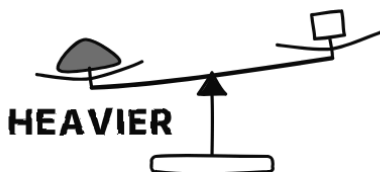
✗ STAHL

**METAL
=
EARTH
+ PHLOGISTON**

**ON BURNING,
PHLOGISTON LEAVES**

✓ LAVOISIER

**EARTH
=
METAL
+ OXYGEN**



Stahl Against Lavoisier

Lavoisier proved with the help of the balance that every rusting of metals, or oxidation and burning, is accompanied by an increase in weight at the expense of the air. He therefore accepted the natural supposition that the heavier body is more complex than the lighter one. Here is the famous experiment made by Lavoisier in 1774, which laid an indisputable foundation for an opinion in many respects opposite to Stahl's teaching. Lavoisier poured 4 ounces of pure mercury into a glass retort A. The neck of the retort was bent, as shown in the figure, and was dipped into a vessel KS, also filled with mercury. The projecting end O of the retort was covered with a glass bell jar FQ. Before the experiment the weight of all the mercury taken was determined, and the whole volume of air remaining in the apparatus, that is, in the upper parts of the retort and under the bell

jar. Here it was precisely very important to determine the quantity of air, in order to learn what part it plays in the oxidation of mercury: in Stahl's opinion, when mercury is oxidised phlogiston is given off into the air, while Lavoisier held that mercury, in being oxidised, absorbs part of the air, and therefore it had to be learned whether the quantity of air increases or decreases when a metal is oxidised. That is why it was important to measure the volume of air before and after the experiment. To achieve this measurement it was necessary to know the whole capacity of the retort, the volume of mercury poured into it, the volume of the bell jar up to the mark to which air stood in it, and also the temperature and pressure of the air at the time of its measurement. By putting all these data together, one could learn the volume of the air left in the apparatus and cut off from the rest of the air. Having prepared the apparatus in this way, Lavoisier heated the retort with the mercury for twelve days to a temperature close to the boiling point of the mercury. In the process the mercury became covered with a multitude of red scales, that is, it was oxidised, or turned into an earth (its calx). This was the red mercury oxide that was spoken of above (example 3). After twelve days the apparatus was cooled, and then it could be seen that the volume of air had decreased during the experiment, which served to refute the opinion of the German scientist. Of the 50 cubic inches of air taken, only 42 remained. Lavoisier's experiment led to other conclusions no less important. The weight of the air taken decreased by as much as the weight of the mercury increased on oxidation, that is, part of the air was not destroyed, but only combined with the mercury. This part of the air can be set free again from red mercury oxide and has, as we have seen (example 3), properties different from air. It was named oxygen. The part of the air that remained in the apparatus and did not combine with the mercury does not oxidise metals and is quite unable

to support either burning or breathing, so that a lighted splinter goes out at once when dipped into the gas left in the bell jar: "it goes out in the remaining gas as if dipped into water," writes Lavoisier in his memoir. This gas is called nitrogen. Thus air is not a simple body, but consists of two gases, oxygen and nitrogen; consequently the opinion that air is an elementary substance is wrong. In burning and in the oxidation of metals the oxygen of the air is absorbed. The earths that arise through the oxidation of metals are bodies composed of oxygen and metals. By mixing oxygen with nitrogen we shall again obtain the same air as we had before. It was also proved by direct experiment that when an oxide is reduced by charcoal, the oxygen contained in the oxide passes to the charcoal and gives the very gas that is obtained when charcoal burns in air. Consequently this gas too is a complex body, made up of charcoal and oxygen, as oxides are made up of metals and oxygen.

12 DAYS

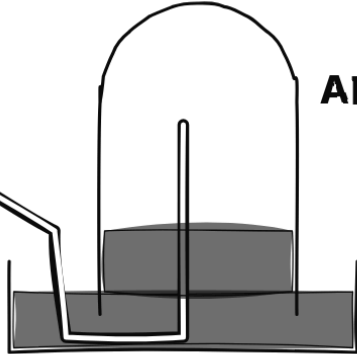
**50 IN³
→ 42 IN³**

MERCURY



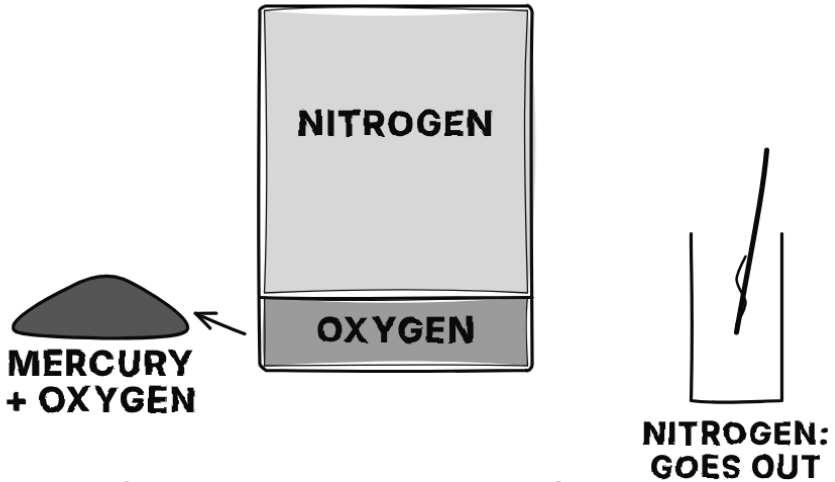
**RED
SCALES**

AIR



Twelve Days of Heating Mercury

AIR



CHARCOAL + OXYGEN → GAS

Air Is Two Gases

Questions

1. The alchemists got lead from galena and then silver from lead. Why did they wrongly conclude that lead turns into silver?
 - a. Because they rarely weighed, and so did not see that the silver had been in the lead all along
 - b. Because the silver they made was really a kind of lead
 - c. Because galena contains no lead at all
 - d. Because they used too little heat to separate the metals

2. According to Stahl, why does charcoal turn an earthy oxide back into metal?
 - a. Because charcoal takes oxygen away from the oxide
 - b. Because charcoal is rich in phlogiston and gives part of it to the earthy substance
 - c. Because charcoal is heavier than the oxide
 - d. Because heating alone turns any earth into metal
3. In Lavoisier's twelve-day experiment, why was it so important to measure the volume of air before and after?
 - a. To find the boiling point of mercury
 - b. To check that the bell jar did not leak mercury
 - c. To decide whether oxidation gives something off into the air, as Stahl said, or takes part of the air up
4. What did the gas left under the bell jar after Lavoisier's experiment show about air?
 - a. That air is a single elementary substance
 - b. That air is partly made of mercury vapour
 - c. That the air had been destroyed by the heat
 - d. That air consists of two gases, one taken up by the mercury and one that supports neither burning nor breathing

Answers

1. **a)** They paid little attention to quantities; had they studied it in detail, they would have found that lead only contains a share of silver and, once this is separated, can give no more.
2. **b)** In Stahl's view charcoal reduces earthy substances precisely because it is rich in phlogiston and gives them part of it.

3. c) In Stahl's opinion phlogiston is given off into the air, while Lavoisier held that mercury absorbs part of the air, so it had to be learned whether the air increases or decreases.

4. d) The remaining gas, nitrogen, does not oxidise metals and puts out a flame, while the part taken up was oxygen; so air is not a simple body but consists of two gases.

Worked examples

How much air the mercury took Lavoisier shut 50 cubic inches of air in with the mercury and heated it for twelve days; afterwards only 42 cubic inches remained. How much air combined with the mercury, and what share of the air was that?

The air that combined is the difference between the air before and after:
 $50 - 42 = 8$ cubic inches.

Its share of the air taken is 8 out of 50, that is $8/50$.

$8/50 = 16/100$, so about 16 parts in every hundred.

The air did not increase, as Stahl's phlogiston would require, but decreased, because part of it combined with the mercury.

Answer: 8 cubic inches, about 16 parts in a hundred of the air taken

Practice

1. In Lavoisier's experiment the mercury gained weight as it became red mercury oxide. By how much, compared with the weight lost by the air, and what does that tell you?

Hint: Use the law that matter is neither created nor lost, applied to the mercury and the air together.

Answer: Exactly as much as the air lost. So part of the air was not destroyed but combined with the mercury; this part, oxygen, can be set free again from red mercury oxide.

2. Explain in your own words why Lavoisier considered scale (an oxide) more complex than the metal, while Stahl considered the metal more complex.

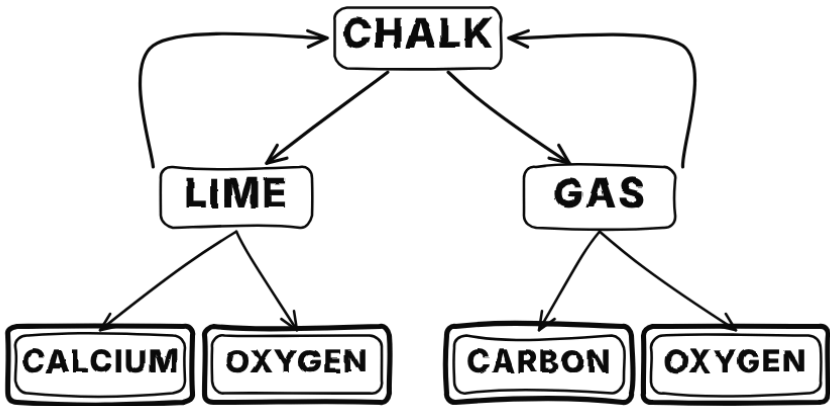
Hint: Think about what each of them believed passes between the metal and the air.

Answer: Stahl thought a metal was an earthy oxide plus phlogiston, and that phlogiston leaves in oxidation, so the metal was the complex body. Lavoisier weighed and found that oxidation always increases the weight at the expense of the air, so the heavier body, the oxide, is metal plus oxygen and is the more complex one.

Introduction

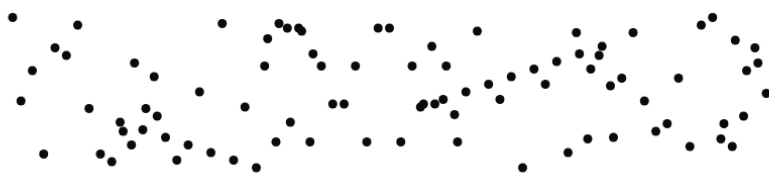
Numerous examples of the combination and decomposition of bodies show that most of the bodies we have to deal with are complex bodies, made up of several other bodies. By strongly heating chalk (like the copper carbonate in the second example), we obtain lime and the same carbonic acid gas that is produced when charcoal burns. By bringing lime into contact with this gas (and with water), at ordinary temperature we again obtain a complex lime carbonate substance similar to chalk; consequently chalk is a complex body; but the substances from which it can be obtained are not simple substances either, because carbonic acid gas is formed by the combination of carbon with oxygen, and lime arises through the oxidation of a particular metal called calcium. By breaking substances up in this way into their component parts, one comes at last to such as can no longer be divided by any possible means into two or more others, or be composed out of anything. Such substances can only combine with one another or act on other bodies. Such substances, which can be neither composed out of anything nor decomposed into any others, are called simple. Thus all homogeneous substances can be divided into simple and complex. This notion was introduced into science, and has been kept in it, since the time of that same Lavoisier. The number of simple bodies is very small in comparison with the number of complex bodies they form. At the present time about seventy-five simple bodies are known with positive certainty. Some of them are met with very rarely in nature or are found in insignificant quantity; while the number of simple bodies with whose compounds we usually deal in everyday life is not more than 25.

LIME + GAS → CHALK

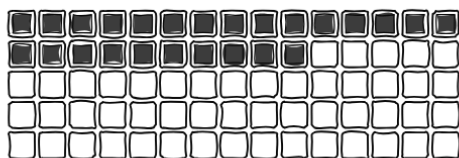


SIMPLE

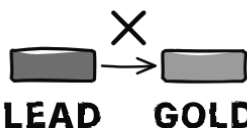
Breaking Down to the Simple



COMPLEX BODIES: COUNTLESS



**75 SIMPLE
25 EVERYDAY**



EACH: CONSTANT

About Seventy-Five Simple Bodies

Simple bodies are incapable of turning into one another; at least, not one case of such a transformation has been noticed so far, and therefore at the present time it is impossible to turn one metal into another; and so far, despite a mass of efforts, not one fact has been found that would in the least justify the idea that the undoubtedly known simple bodies, such as oxygen, iron, sulphur and the like, are complex. Consequently simple bodies, by the very notion of them, are incapable of reactions of decomposition. Therefore, as a consequence of the law of the eternity of matter and of the notion of a simple body, it can be deduced that the quantity of each simple body remains constant in all chemical transformations. Consequently the equation expressing the law of the eternity of matter acquires a new and still more important meaning. If we know the quantities of the simple

bodies present in the acting bodies, and if from these bodies a series of new complex bodies arises by way of chemical change, then these can contain only the same quantity of each of the simple bodies as there was in the acting bodies. The essence of chemical transformations comes down to the study of what each simple body is combined with, and how, before and after the transformation.

To be able to express various chemical transformations by equations, it has been agreed to denote each simple body by one or two initial letters of the Latin name of the simple body. Thus, for example, O denotes oxygen, which is called Oxygenium in Latin; N denotes nitrogen, Nitrogenium; Hg, mercury, Hydrargyrum; Fe, iron, Ferrum; and so on for each simple body, as will be seen from the table given further on. A complex body is denoted by placing side by side the letters that denote the simple bodies of which it consists. For example, HgO denotes red mercury oxide, which shows that it is composed of oxygen and mercury. Besides this, to the sign of each simple body there corresponds a certain relative quantity of it by weight, called its proportion, or the weight of its atom, so that the chemical formula of a complex body denotes not only the quality of the simple bodies of which the complex body consists, but also the quantitative content of each simple body. Every chemical process can be expressed by an equation made up of the formulas that correspond to the bodies that act and are produced. The quantity by weight of the simple bodies in every chemical equation must be equal in both parts of the equation, because no simple body is either newly formed or lost in chemical transformations.

O	OXYGENIUM		
N	NITROGENIUM		
Hg	HYDRARGYRUM		HgO
Fe	FERRUM		RED OXIDE

ATOM WEIGHTS

Signs for the Simple Bodies

On the following page the more or less well-known simple bodies are listed and the signs corresponding to them are given, while in the preface a table is given of the simple bodies, their signs, and their proportions, or the weights of the atoms, corresponding to the sign of the simple body; and in the further exposition we shall see the grounds for judging the atomic weight of simple bodies. For now we shall only remark that a complex body containing the simple bodies A and B is denoted by the formula A_nB_m , where m and n are the coefficients, or multipliers, with which the proportions of the simple bodies enter into the composition of the body. If we denote the proportion of body A by a, and that of body B by b, then the composition of the body A_nB_m will be expressed thus: it contains na of body A and mb of body B; consequently in 100 parts of our complex

body there are $na \cdot 100 / (na + mb)$ percentage parts by weight of the simple body A, and $mb \cdot 100 / (na + mb)$ of the other simple body. It is clear that by means of the formula we know the relative content of each simple body, and consequently, if the real weight of a complex body is given, the real weight of the simple bodies contained in it will be seen from its formula. For example, the formula NaCl of common salt shows (since Na = 23 and Cl = 35.5) that in 100 parts of it there are 39.3 per cent of sodium and 60.7 of chlorine.

$$A_n B_m$$

N, M: MULTIPLIERS

$$\% A = \frac{na \cdot 100}{na + mb}$$

$$\text{NaCl} : \text{Na} = 23, \text{Cl} = 35.5$$



$$\text{Na } 39.3 \%$$

$$\text{Cl } 60.7 \%$$

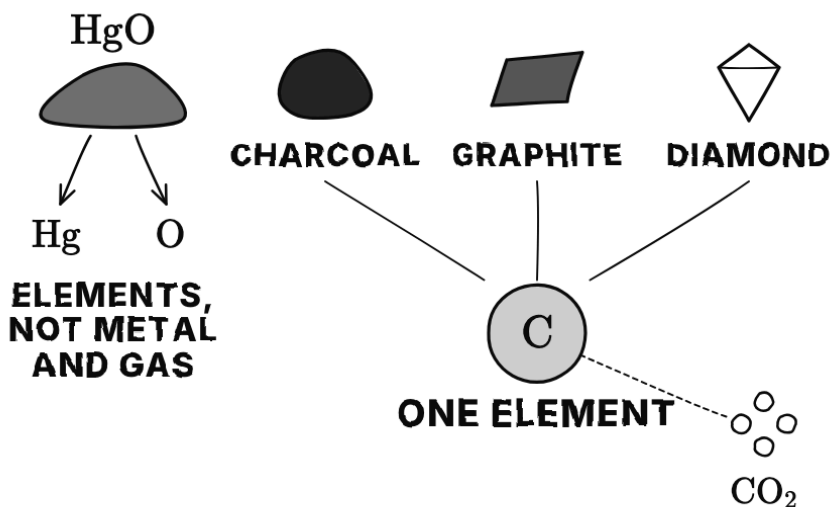
$$23 \div 58.5 = 0.393$$

Percent from a Formula

By what has been said above the notion of chemical transformations is clearly limited: from bodies of a given quality not all possible bodies can be obtained, but only such as contain the very same simple bodies. But even with this first limitation the number of diverse

compounds that can be formed is still infinitely great. Only a comparatively limited number of compounds has been subjected to study and description. Anyone setting to work can easily discover new complex substances not yet obtained; many such newly obtained bodies are already foreseen by science. Science consists in grasping the uniformity that lies hidden in this multitude of complex bodies; its aim is to understand the laws that govern their formation and properties. After the notion of simple bodies was established, the immediate aim of chemistry became the determination of the properties of complex bodies on the basis of determining the quantity and quality of the simple bodies that enter into them, the study of the simple bodies themselves, the determination of which complex bodies, and with what properties, can be formed by each simple body, and the understanding of what the bond of simple bodies in various complex substances consists in, and what it is like. The simple body here serves as the starting point, as the primary notion to which all the rest are reduced. If we assert that such and such a simple body enters into the composition of a given complex body, if we say that red mercury oxide contains oxygen, we do not mean by this that oxygen, as a gaseous substance, is contained in mercury oxide, but only wish to express the transformations of which red mercury oxide is capable; that is, we mean that mercury and oxygen can be obtained from red mercury oxide and that it can give them up to various other bodies; in a word, we wish to express only the transformations of which mercury oxide is capable. Putting it briefly, we may say that the composition of a complex body is the expression of the transformations of which it is capable. In this respect it is useful to make a clear distinction between the notion of a simple body as a separate homogeneous substance, and the notion of it as a material part, or element, of complex substances. Red mercury oxide contains not two simple bodies, a

metal and a gas, but two elements, mercury and oxygen, which, when separate, give the metal and oxygen gas. It is not mercury as a metal, nor oxygen in its gaseous form, that is contained in red mercury oxide: it contains only the substance of these simple bodies, as water vapour contains only the substance of ice, but not ice itself, or as bread contains the substance of grain, but not the grain itself. One can form an idea of the existence of an element without knowing the simple body itself, by studying only its compounds and knowing that under all possible circumstances they give substances not identical with other compounds known to us. Thus, for example, fluorine was long not known by itself, and yet it had to be recognised as an element, because its compounds with other simple bodies were known, and the difference of these compounds from all other similar complex bodies had been established. To grasp still more clearly the difference between the notions of a simple body and an element (or radical, as Lavoisier said), one must note that complex bodies also form new, still more complex compounds. From these new compounds the original complex body can often be extracted by exactly the same means by which simple bodies are extracted from their corresponding compounds. Moreover, many simple bodies exist in various modifications, while a simple element is something not subject to change. Thus carbon appears as charcoal, graphite and diamond, which are different bodies, and simple ones at that, but their element is one. The same carbon is contained in carbonic acid gas too, but there is neither charcoal, nor graphite, nor diamond in it.



Simple Body and Element

Questions

1. Why does the quantity of each simple body stay constant in every chemical transformation?
 - a. Because simple bodies never take part in reactions
 - b. Because matter is never created or lost, and simple bodies cannot be decomposed or turned into one another
 - c. Because the balance cannot weigh simple bodies separately
 - d. Because complex bodies always contain the same simple bodies in the same amounts

2. What does a chemical formula such as NaCl tell you beyond which simple bodies a substance contains?
 - a. How the substance looks and tastes
 - b. At what temperature the substance decomposes
 - c. How much of each simple body it contains by weight, through the weights of their atoms
3. When we say that red mercury oxide contains oxygen, what do we mean?
 - a. That mercury and oxygen can be obtained from it and that it can give them up to other bodies
 - b. That bubbles of oxygen gas are trapped inside the red powder
 - c. That it is a mixture of liquid mercury and oxygen gas
 - d. That it will turn into oxygen if left in air
4. Charcoal, graphite and diamond are different simple bodies. What do they have in common?
 - a. They are all complex bodies of carbon and oxygen
 - b. They are all found in carbonic acid gas
 - c. They have the same properties but different colours
 - d. They are modifications of one element, carbon

Answers

1. **b)** It follows from the law of the eternity of matter together with the notion of a simple body, which can be neither decomposed nor turned into another.
2. **c)** To the sign of each simple body there corresponds a relative quantity by weight, so the formula gives the quantitative content of each simple body

too.

3. a) We only wish to express the transformations of which red mercury oxide is capable: the composition of a complex body is the expression of the transformations of which it is capable.

4. d) Many simple bodies exist in various modifications, while the element is not subject to change: charcoal, graphite and diamond are different bodies, but their element is one.

Worked examples

Percentages in common salt Common salt has the formula NaCl , with $\text{Na} = 23$ and $\text{Cl} = 35.5$. What percentage of it by weight is sodium, and what percentage is chlorine?

In the formula A_nB_m here A is Na and B is Cl, each taken once, so $n = 1$ and $m = 1$.

The weight of one formula of salt is $na + mb = 23 + 35.5 = 58.5$.

Sodium makes up $na \cdot 100 / (na + mb) = 23 \times 100 / 58.5$, which is about 39.3 per cent.

Chlorine makes up $mb \cdot 100 / (na + mb) = 35.5 \times 100 / 58.5$, which is about 60.7 per cent; the two add up to 100.

Answer: 39.3 per cent sodium and 60.7 per cent chlorine

Practice

1. A chemist has 200 grams of pure common salt, NaCl , with $\text{Na} = 23$ and $\text{Cl} = 35.5$. How many grams of chlorine does it contain?

Hint: Find the share of chlorine in salt first, then apply it to the real weight.

Answer: About 121.4 grams. Chlorine is $35.5/58.5$ of the salt, about 60.7 per cent, and 60.7 per cent of 200 grams is about 121.4 grams.

2. Chalk, heated, gives lime and carbonic acid gas, and lime with this gas gives chalk again. Explain why this shows chalk is complex, and why lime and the gas are not simple bodies either.

Hint: Ask of each substance whether it can be decomposed or composed from others.

Answer: Chalk can be broken into two other substances and made again from them, so it is complex. But carbonic acid gas is formed from carbon and oxygen, and lime from the oxidation of the metal calcium, so they too can be made from other substances and are complex. Only substances that can be neither decomposed nor composed are simple.

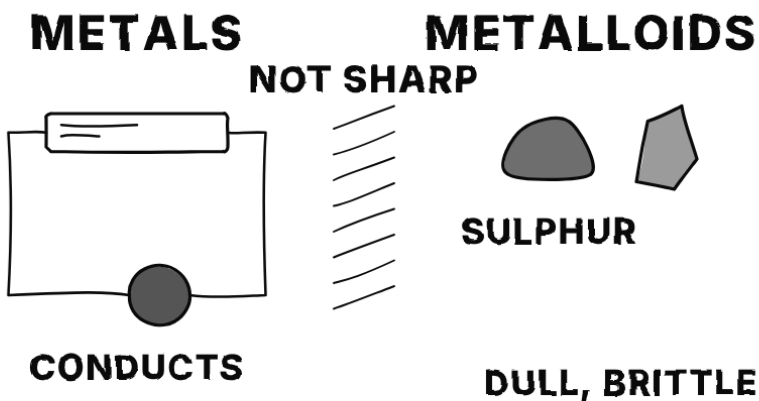
3. Fluorine was long unknown as a separate substance, yet it was counted as an element. Explain how that was possible.

Hint: Think about what an element is known by: the simple body itself, or its compounds?

Answer: An element can be recognised from its compounds alone. Compounds of fluorine with other simple bodies were known, and they differed from all other similar complex bodies, so they had to contain a distinct element, even before the simple body was obtained.

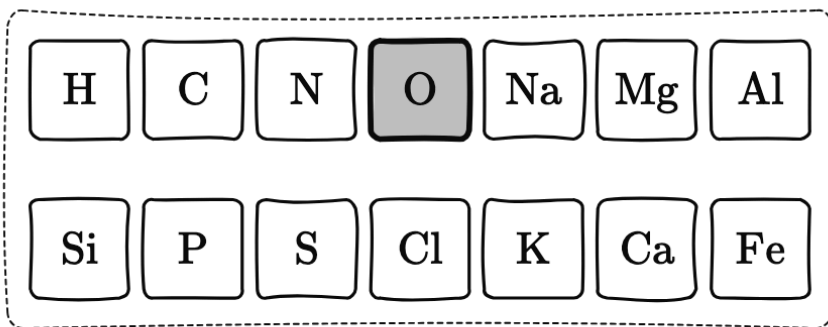
Introduction

Many simple bodies, though not all, have the particular lustre, opacity, malleability, and high conductivity for heat and electricity that are proper to metals and to their compounds with one another, which are called alloys. But far from all simple bodies are metals. Simple bodies that do not have the physical features proper to metals are called metalloids. In sharp examples the two classes of simple bodies are clearly distinguished, but in many particular cases the difference is not sharp, and therefore it cannot serve as the basis for an exact division of simple bodies into two groups.



ABOUT 80 SIMPLE BODIES

In any case, the notion of elements and simple bodies forms the basis of chemical knowledge, and if we give here, from the very beginning, a list of the simple bodies, we wish by this to indicate the state of present knowledge on this subject. Altogether about 80 simple bodies are recognised so far, but some of them (about 6) are met with so rarely in nature and have been obtained in such small quantities that knowledge of them is sometimes insufficient and incomplete. The commonly occurring bodies of nature contain a very small number of simple bodies. The study of these latter is more perfect than that of the others, if only because experiments and observations on them could be made by a greater number of investigators. The simple bodies most widespread in nature are:



The Commonest Fourteen

Hydrogen, H: in water and in organisms. Carbon, C: in organisms, coal and limestones. Nitrogen, N: in the air and in organisms. Oxygen, O: in the air, water and earth; its mass is the greatest. Sodium, Na: in common salt and in many stones. Magnesium, Mg: in sea water and in many stones. Aluminium, Al: in stones and clay. Silicon, Si: in sand, clay and stones. Phosphorus, P: in bones, the ash of plants, and soil. Sulphur, S: in pyrites, gypsum and sea water. Chlorine, Cl: in common salt and in sea water. Potassium, K: in stones, the ash of plants, and saltpetre. Calcium, Ca: in limestones, gypsum and organisms. Iron, Fe: in soil, iron ores and organisms.

Besides these, the following simple bodies, or their compounds, though not very widespread in nature, are used in everyday life or in technology:

Lithium, Li: in medicine as Li_2CO_3 , and in photography as LiBr. Boron, B: borax, $\text{B}_4\text{Na}_2\text{O}_7$, and boric acid, BH_3O_3 . Fluorine, F: fluorspar, CaF_2 , and hydrofluoric acid, HF. Chromium, Cr: chromic anhydride, CrO_3 , and potassium bichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. Manganese, Mn: manganese peroxide, MnO_2 , and chameleon, MnKO_4 . Cobalt, Co: in smalt and in blue glasses. Nickel, Ni: other metals are coated with it, that is, nickel-plated. Copper, Cu: the well-known red metal. Zinc, Zn: in sheets, in galvanic cells, and in brass. Arsenic, As: white arsenic, a poison, As_2O_3 . Bromine, Br: a brown volatile liquid; sodium bromide, NaBr. Strontium, Sr: in Bengal lights, SrN_2O_6 . Silver, Ag: the well-known white metal. Cadmium, Cd: a white metal; a yellow paint, CdS. Tin, Sn: a well-known metal. Antimony, Sb: in alloys, for example in printing type. Iodine, J: in medicine and photography, as free iodine and as KJ. Barium, Ba: as an admixture to white lead, and in heavy spar, BaSO_4 . Platinum, Pt, gold, Au, mercury, Hg, and lead,

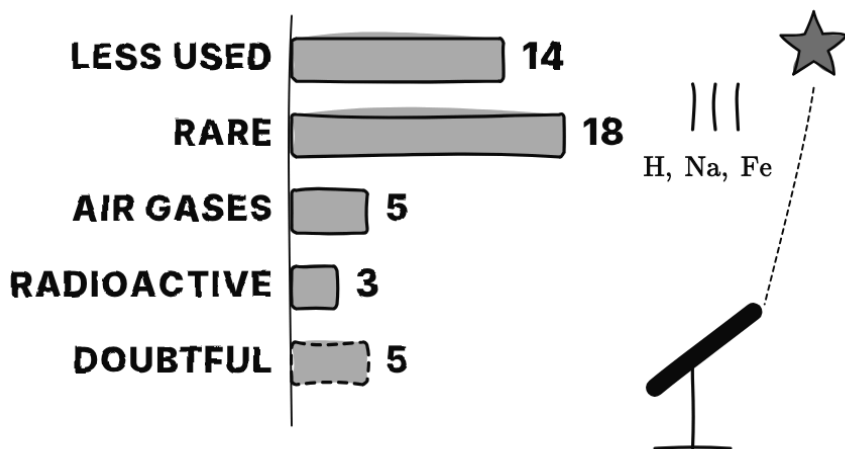
Pb: generally known metals. Bismuth, Bi: in medicine and in easily fusible alloys.

USED IN EVERYDAY LIFE

Li	B	F	Cr	Mn	Co	Ni	Cu
Zn	As	Br	Sr	Ag	Cd	Sn	Sb
I	Ba	Pt	Au	Hg	Pb	Bi	

Used in Daily Life

Less used, but well known, and, though in small quantities, met with fairly often in nature, are the compounds of the following simple bodies:



The Rest of the List

Beryllium, titanium, vanadium, selenium, zirconium, molybdenum, palladium, cerium, tungsten, osmium, iridium, thallium, thorium and uranium.

Still more rarely met with in nature, and having no use in practice, but investigated with some completeness, are the compounds of the following elements:

Scandium, gallium, germanium, rubidium, yttrium, niobium, ruthenium, rhodium, indium, tellurium, caesium, lanthanum, neodymium, praseodymium, samarium, ytterbium, erbium and tantalum.

A special group of simple bodies is then formed by the gaseous substances discovered by Ramsay, which enter in small quantity into the composition of the air and differ from all others in that so far it has not been possible to obtain a single compound of them with other elements: helium, neon, argon, krypton and xenon. Then there is some ground for recognising the independence of the metals actinium, polonium and radium (discovered by Madame Curie), which enter into the composition of the so-called radioactive compounds that form a small admixture to the natural compounds of uranium and thorium.

Over and above these 77, the following are counted among the simple bodies: gadolinium, terbium, thulium, holmium, carolinium and several others. But their properties and compounds, because of their great rarity in nature, are still little known, and even the independence of some of them has not been finally established.

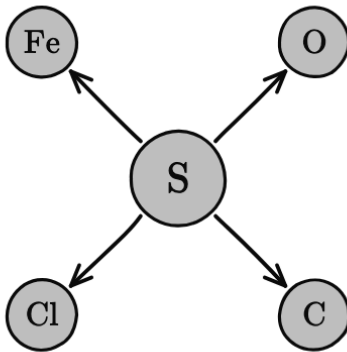
The presence of many of the commonest simple bodies on earth (for example hydrogen, sodium, magnesium and iron) has been proved beyond doubt on heavenly bodies remote from us by means of the investigation of their light. This convinces us that the form of matter which appears on earth as simple bodies is widely spread in the universe. But why the mass of some simple bodies in nature is greater than that of others, we do not yet know.

The ability of each simple body to combine with other elements and to form with them complex bodies of greater or lesser stability, inclined to give new, still more complex compounds, makes up the fundamental character of each element. Thus, for example, sulphur combines easily with metals, with oxygen, with chlorine and with carbon, while silver and gold enter into compounds with difficulty,

and many of the compounds arising from them are unstable and easily decompose on strong heating. The cause, or force, that impels substances to chemical changes must be regarded at the same time as the cause that holds dissimilar elements together in combination and gives the substances formed a certain degree of stability. This cause, or force, is called affinity (*affinitas*, *affinité*, *Verwandtschaft*), or chemical affinity. Since this force must be regarded exclusively as attractive, like gravitation, many, for example Bergman at the end of the eighteenth century and Berthollet at the beginning of the nineteenth, supposed that affinity may in essence be identical with universal gravitation, and that the whole difference between them depends only on the fact that the latter acts at noticeable distances, whereas affinity shows itself only at the smallest distances. But chemical affinity cannot be fully identified with universal attraction, for the latter depends only on mass and distances, and not on the quality of the substance, on which affinity depends strongly. Nor can it be fully identified with cohesion, which gives homogeneous solid bodies their crystalline form, elasticity, hardness, toughness and similar properties, and which in liquids determines their surface, the formation of drops, the rise in capillary tubes and similar properties; for affinity acts between dissimilar substances, and cohesion between similar ones, although both act only at imperceptibly small distances (on contact) and have much in common. The chemical force that makes one substance penetrate another cannot be fully identified even with those attractive forces that make dissimilar bodies stick together or hold them close to each other, for example two flat polished surfaces of solid bodies, or that make liquids wet solid bodies and stick to their surface, or make gases and vapours condense on the surface of solid bodies. These forces must not be confused with chemical ones, because under the action of the latter one body is

penetrated by another and a new one is formed, which does not happen in sticking together.

AFFINITY



EASILY



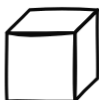
HARDLY

Some Join Easily, Some Hardly



GRAVITY

**ONLY
MASS**



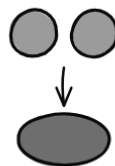
COHESION

**ONE BODY
HOLDS
TOGETHER**



STICKING

**EACH
STAYS
ITSELF**



CHEMICAL

**SOMETHING
NEW**

Affinity Is Not Gravity or Cohesion

But it is evident that the forces determining the cohesion of dissimilar bodies represent a transition from mechanical forces to chemical ones, because they act only on full contact. For a long time, especially in the first half of the nineteenth century, chemical attraction and chemical forces were identified with electrical ones. A close connection between them certainly exists, since electricity is developed in chemical interactions, and it, for its part, is able to influence chemical processes sharply; for example, complex bodies are decomposed by the action of a galvanic current. But exactly the same connection of chemical phenomena with thermal ones (heat is developed in chemical phenomena, and bodies can be decomposed by heat) shows only the unity of the forces of nature, the ability of some forces to produce others, to turn into them and to modify them. And

therefore the identification of chemical forces with electrical ones could not stand the test of experiment. Since of all the molecular phenomena of nature only thermal phenomena are now known with the greatest (relative) perfection and completeness, and precisely they have been reduced to the simplest, fundamental mechanical notions (of energy, equilibria and motions), which since the time of Newton can also be subjected to strict mathematical analysis, it is quite natural that there should be a striving, expressed especially in recent decades, to bring chemical notions into strict relation with the studied phenomena of heat, though without any identification of chemical phenomena with thermal ones. The nature of chemical forces is as hidden from us to this day as the nature of universal gravitation; but just as, without knowing the nature of the latter, by applying mechanical notions, astronomical phenomena became subject to exact generalisation and to the detailed prediction of a multitude of particulars, so, without knowing the nature of chemical affinity, by means of the successes of the mechanical theory of heat, there is hope of achieving considerable success in the study of chemistry. But to this day this part of chemical knowledge has not yet been fully worked out, and therefore, forming a current task of science, it is developed in more detail in a special part of chemistry, called either theoretical or physical chemistry, and best designated by the name chemical mechanics. Since in this field of chemistry there are assumed to be already known not only the diverse homogeneous substances obtained so far, but also the chemical transformations that take place with them and the phenomena (thermal and all others) that accompany them, it is possible to approach chemical mechanics only after becoming acquainted with the fundamental chemical notions and substances, which forms the chief aim of our work.

Questions

1. Why can the division of simple bodies into metals and metalloids not serve as an exact classification?
 - a. Because in many particular cases the difference between the two classes is not sharp
 - b. Because all simple bodies are really metals
 - c. Because metalloids cannot be obtained in pure form
 - d. Because alloys belong to both classes
2. What does the study of the light of distant heavenly bodies show about simple bodies?
 - a. That the heavenly bodies are made of quite different simple bodies from the earth
 - b. That the commonest simple bodies of the earth are found there too, so this form of matter is spread through the universe
 - c. That hydrogen exists only on the stars
 - d. That it explains why some simple bodies are more abundant than others
3. Why can chemical affinity not be fully identified with universal gravitation?
 - a. Because affinity acts at great distances and gravitation does not
 - b. Because gravitation is repulsive and affinity attractive
 - c. Because gravitation depends only on mass and distance, while affinity depends strongly on the quality of the

substances

4. Two polished plates of different metals stick together when pressed. Why is this not a chemical action?
 - a. Because the plates are both metals
 - b. Because they are held only by electricity
 - c. Because sticking happens only between similar bodies
 - d. Because neither body penetrates the other and no new substance is formed

Answers

1. **a)** In sharp examples the two classes are clearly distinguished, but in many particular cases the difference is not sharp.
2. **b)** Hydrogen, sodium, magnesium, iron and others have been found on remote heavenly bodies through their light, so the form of matter seen on earth as simple bodies is widely spread in the universe.
3. **c)** Universal attraction depends only on mass and distances, not on the quality of the substance, on which affinity depends strongly.
4. **d)** Under chemical forces one body is penetrated by another and a new one is formed, which does not happen in sticking together.

Practice

1. Explain in your own words how chemical affinity differs from cohesion, and what the two have in common.

Hint: Ask between which kinds of substances each force acts, and at what distances.

Answer: Cohesion acts between parts of the same substance and gives solids their form, hardness and elasticity and liquids their drops and

surface; affinity acts between dissimilar substances and makes them form a new substance. Both act only at imperceptibly small distances, on contact.

2. In the nineteenth century chemical forces were thought to be electrical. Why, according to the passage, could that view not stand, even though electricity and chemical action are closely connected?

Hint: Compare the connection between chemical action and electricity with the connection between chemical action and heat.

Answer: Electricity is developed in reactions and a galvanic current decomposes compounds, but heat has exactly the same kind of connection: it is developed in reactions and decomposes bodies. Such connections show only the unity of the forces of nature, that one force can produce and turn into another, not that chemical forces are electrical ones; and the identification failed the test of experiment.

3. Sulphur combines easily with metals, oxygen, chlorine and carbon, while silver and gold combine with difficulty and their compounds decompose easily on heating. What does this tell you about each element, in the passage's terms?

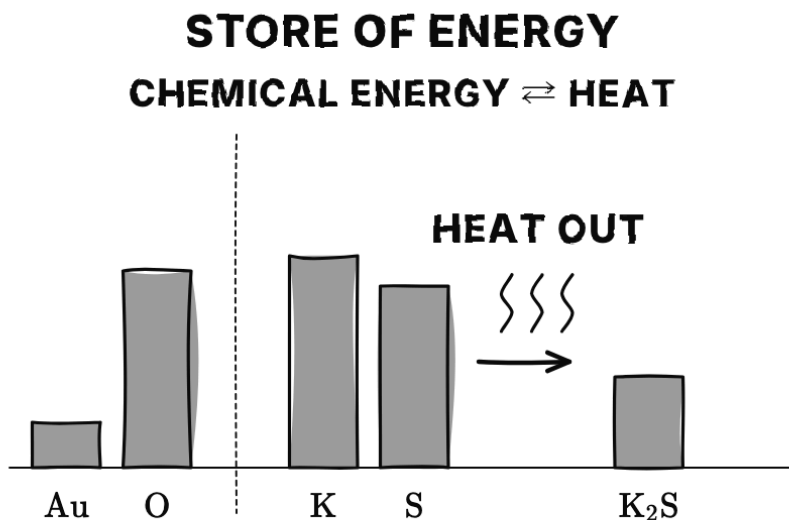
Hint: Think about what the passage calls the fundamental character of an element.

Answer: The ability to combine with other elements, and the stability of the compounds formed, make up the fundamental character of each element. Sulphur has a strong tendency to combine, silver and gold a weak one, and this difference is ascribed to chemical affinity, the force that both drives reactions and holds the compounds together.

Introduction

Since the chemical changes of matter come from internal forces proper to it, since chemical phenomena consist without fail in the motion of material parts, and since the study of mechanical and physical phenomena establishes the law of the eternity of forces, or of the conservation of energy, it is unavoidable to recognise in substances (and in particular in the elements) a store of chemical energy, or of invisible motion, impelling them to enter into reactions. If heat is evolved in a reaction, it means that part of the chemical energy can pass into thermal energy; if heat is absorbed in a reaction, it can (become hidden and) partly pass into chemical energy. The store of force, or energy, for forming new complex bodies may at last, after several combinations accomplished with loss of heat, decrease so far that unenergetic complex bodies are obtained; but they can sometimes combine with an energetic simple or complex body and again give more complex bodies possessing the ability for chemical interactions. Among the simple bodies, gold, platinum and nitrogen have little energy; potassium, chlorine and oxygen have a very considerable degree of energy. But energy does not show itself towards all bodies either. Bodies dissimilar to one another, if they enter into combination, often form substances of diminished energy. Thus potassium and sulphur burn easily in air if they are first strongly heated; but once they have combined with each other, the complex body produced, although capable of oxidation, does not burn in air as its separate component parts do. Part of the energy of the potassium and the sulphur was given off as heat when they combined with each other. Just as part of the store of heat is absorbed or given off in

passing from one state into another, so in combinations, decompositions and all chemical processes there takes place a change in the store of chemical energy, and together with it heat is given off and absorbed.



For understanding chemical phenomena in the mechanical sense, that is, for studying the course of chemical phenomena, the following must be regarded as especially important at the present time: 1) the knowledge of stoichiometry, that is, of that part of chemistry which studies the quantitative relations by weight and by volume between reacting substances; 2) the distinction of the various kinds and classes of chemical interaction; 3) the study of the change of properties with the change of composition; 4) the study of the phenomena

accompanying chemical transformations; and 5) the generalisation of the conditions in which reactions take place. As regards stoichiometry, this field of chemistry has been worked out with great completeness, and laws have been found in it (by Dalton, by Avogadro and Gerhardt, and others) that penetrate so deeply into all parts of chemistry that its whole present state can be characterised as the epoch of their detailed application to particular cases. The expression of the quantitative (weight and volume) composition of bodies is to this day the most important task of chemical investigations, and therefore the whole further exposition of the subject is subordinated to the stoichiometric laws. Even the very meaning of reactions of combination, decomposition and displacement, as we shall see further on, has acquired a particular, new character under the influence of the development of exact notions of the quantitative relations of the bodies entering into reaction. Moreover, in this sense a new division of complex bodies, which had not existed before, was born: into definite and indefinite compounds. Even at the beginning of the nineteenth century Berthollet did not make this distinction. But Proust showed that a great many complex bodies contain the component parts from which they arise, or into which they break up, in a perfectly exact, definite proportion by weight, unchanging under any conditions. Thus, for example, red mercury oxide contains 16 parts of oxygen to 200 parts by weight of mercury, which is expressed by the chemical formula HgO . But in an alloy of copper with silver one may add any quantity of the one metal or the other, just as in a solution of sugar in water the relative content of the parts may be varied, and still a homogeneous whole is obtained, with the sum of independent properties. In these latter cases, then, an indefinite chemical compound is formed. Although in nature and in chemical practice (in the laboratory and in the factory) the formation of

indefinite compounds (for example alloys and solutions) plays just as essential a part as the formation of definite chemical compounds, yet since the stoichiometric laws have so far been applied chiefly to the latter, all knowledge of indefinite compounds is less complete, and only in recent years has the attention of many investigators turned to this field of chemistry.

COMPOSITION BY WEIGHT

DALTON · AVOGADRO · GERHARDT

DEFINITE



Hg 200

ALWAYS 200 : 16

INDEFINITE



ANY SHARE

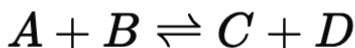
Definite and Indefinite

For chemical mechanics it is very important to distinguish reversible reactions from irreversible ones. Substances that can react with one another at a given temperature give bodies that at the same temperature either can or cannot give back the original substances. Thus, for example, salt dissolves in water at ordinary temperature, but the solution obtained can break up at the same temperature, leaving

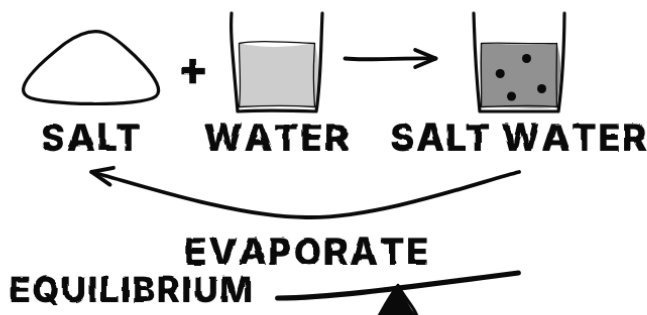
salt and giving off water by evaporation. Carbon bisulphide arises from sulphur and charcoal at a temperature at which it can also give back sulphur and charcoal. Iron at a certain temperature sets free hydrogen from water, forming iron oxide, but this oxide at the same temperature can give iron and water with hydrogen. It is evident that if bodies A and B give C and D, and the reaction is reversible (that is, C and D give A and B), then, taking a definite mass of A and B, or the corresponding mass of C and D, we shall in both cases obtain all four bodies; that is, a chemical equilibrium (or distribution) will set in between the reacting substances. By increasing the mass of one of the substances we shall obtain new conditions of equilibrium, so that reversible reactions provide the possibility of studying the influence of mass on the course of chemical transformations. Many of the reactions that take place with very complex compounds and mixtures may serve as examples of irreversible chemical reactions. Thus many complex substances of organisms (of plants and animals) break up in heat, but at no temperature do the products of the breaking up give back the original substance among themselves. Gunpowder, as a mixture of saltpetre, sulphur and charcoal, gives on burning gases and powder smoke, which at no temperature give back the initial substances. To obtain them, a roundabout way is necessary: combination by residues. If A does not combine directly with B under any conditions, this does not yet mean that they cannot give the compound AB. Often A can be combined with C, and B with D, and if C has a great affinity for D, then the interaction of AC with BD gives not only CD but also AB. Since in the formation of CD the substances A and B, which were in AC and BD, remain in a particular state of being set free, it is supposed that their combination with each other into AB takes place precisely because they meet in this newly set-free state, "at the moment of being set free" (*in statu nascendi*). Thus, for

example, chlorine does not react directly with charcoal, graphite or diamond, which are modifications of free carbon, and yet compounds of chlorine with carbon exist, and many of them are distinguished by their stability. They are obtained by the action of chlorine on hydrocarbons, as residues from the direct reaction of chlorine with hydrogen. The chlorine takes away the hydrogen, and the carbon set free enters, at the moment of being set free, into combination with part of the chlorine, so that in the result the chlorine is found combined with hydrogen and with carbon.

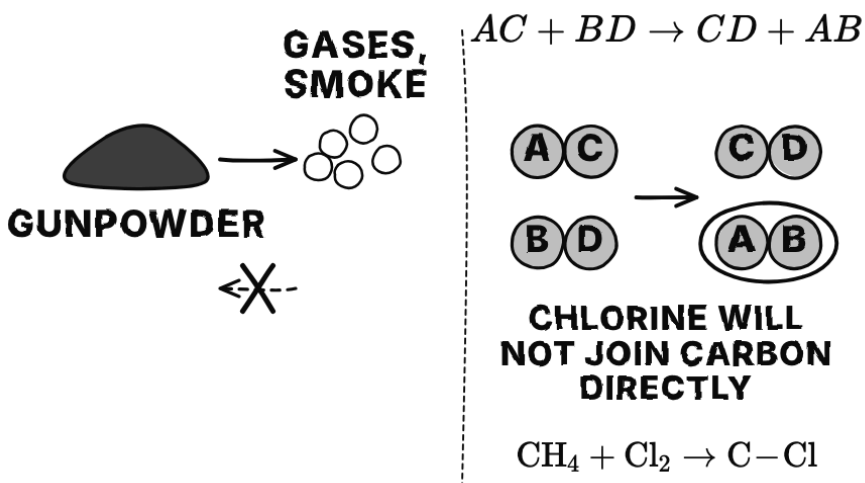
REVERSIBLE



MORE B ↑



Reactions That Go Both Ways



One-Way Changes and Detours

Questions

1. Potassium and sulphur each burn easily in air, but the compound they form does not. Why?
 - a. Because part of their chemical energy was given off as heat when they combined
 - b. Because the compound contains no potassium or sulphur any more
 - c. Because the compound cannot be oxidised at all

- d. Because combining doubled their energy, making them too stable to burn
2. Which of these is an indefinite compound in the sense of the passage?
- a. Red mercury oxide, with 16 parts of oxygen to 200 of mercury
 - b. Common salt, with a fixed formula
 - c. An alloy of copper and silver, to which any quantity of either metal can be added
3. In a reversible reaction $A + B \rightleftharpoons C + D$, what is found if you start from a definite mass of A and B?
- a. Only C and D, because the reaction goes to the end
 - b. All four bodies, because a chemical equilibrium sets in between them
 - c. Only A and B, because the reaction cannot start
 - d. A new fifth body formed at the moment of being set free
4. Chlorine does not react directly with charcoal, graphite or diamond, yet compounds of chlorine and carbon exist. How are they obtained?
- a. By heating chlorine with diamond to a very high temperature
 - b. By mixing chlorine gas with powdered charcoal and waiting
 - c. Through electricity, which forces chlorine and carbon together
 - d. By acting with chlorine on hydrocarbons, so that carbon is set free at the moment it can combine with chlorine

Answers

- 1. a)** Part of the energy of the potassium and the sulphur was given off as heat when they combined, so the compound has diminished energy.
- 2. c)** In an alloy of copper with silver any quantity of either metal can be added and still a homogeneous whole is obtained, so it is an indefinite compound.
- 3. b)** Since C and D also give A and B, starting from either pair we obtain all four bodies: a chemical equilibrium sets in.
- 4. d)** The chlorine takes away the hydrogen, and the carbon set free enters, at the moment of being set free, into combination with part of the chlorine.

Worked examples

Oxygen in red mercury oxide Red mercury oxide contains 16 parts of oxygen to 200 parts by weight of mercury, in a proportion that never changes. How many grams of oxygen are there in 54 grams of red mercury oxide?

The proportion is definite, so every $200 + 16 = 216$ parts of the oxide contain 16 parts of oxygen.

So the share of oxygen in the oxide is $16/216$.

In 54 grams there are $54 \times 16/216$ grams of oxygen.

$54/216 = 1/4$, so this is $16/4 = 4$ grams; the rest, 50 grams, is mercury, keeping the same 16 to 200 ratio.

Answer: 4 grams of oxygen

Practice

1. 100 grams of mercury are wholly turned into red mercury oxide, which contains 16 parts of oxygen to 200 of mercury. How much oxygen is taken up, and what does the oxide weigh?

Hint: Scale the proportion 200 to 16 down to 100 grams of mercury, then use the law of conservation.

Answer: 8 grams of oxygen, since 100 is half of 200 and half of 16 is 8. The oxide weighs $100 + 8 = 108$ grams.

2. Explain in your own words why dissolving salt in water is called a reversible reaction, while the burning of gunpowder is irreversible.

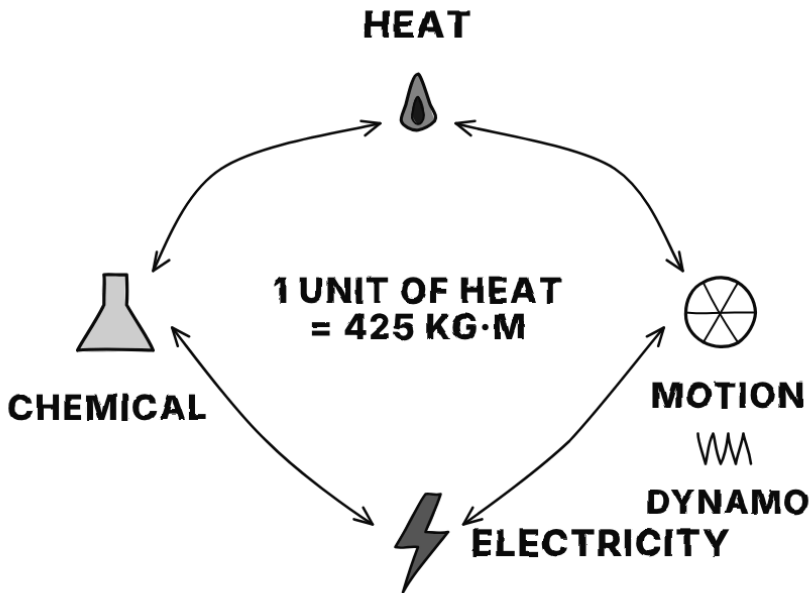
Hint: Ask whether the products can give back the original substances at the same temperature.

Answer: The salt solution can break up again at the same temperature, leaving salt and giving off water by evaporation, so the original substances come back. The gases and smoke of burnt gunpowder give back saltpetre, sulphur and charcoal at no temperature at all, so that reaction is irreversible; the original substances can be had only by a roundabout way.

Introduction

As regards the phenomena accompanying the interaction of bodies, what matters most for chemical mechanics is the circumstance that in chemical processes there arise not only mechanical displacement (motion of parts), heat, light, electrical tension and galvanic current, but that all these agents are themselves able to change chemical transformations. Such reciprocity, or reversibility, depends, of course, on the fact that all the phenomena of nature are only different kinds and forms of motions, visible and invisible (molecular). First sound, and then light, turned out to be in essence vibratory motions, as physics develops and proves beyond doubt. Then the connection of heat with mechanical motion and work ceased to be a supposition and became certain, and the mechanical equivalent of heat (425 kilogram-metres of mechanical work correspond to one kilogram unit of heat, or calorie) gives a mechanical measure of thermal phenomena. It is known that both static and dynamic electricity are obtained by mechanical means (for example in the dynamo machines of Gramme and others), and, conversely, mechanical motion can be produced by a current (in electric motors). Thus, by passing a current through the conductors of a Gramme machine, one can make it rotate, and by rotating it one can obtain a current, that is, demonstrate the reversibility of electricity into mechanical motion. Therefore chemical mechanics must draw the main features of its development from the connection of chemical phenomena with physical and mechanical ones. But, because of its complexity and comparative novelty, this subject has not yet received a harmonious theory or even a satisfactory hypothesis, and therefore in the further exposition we

avoid dwelling on it, leaving this field of physical chemistry as a separate part of our science.

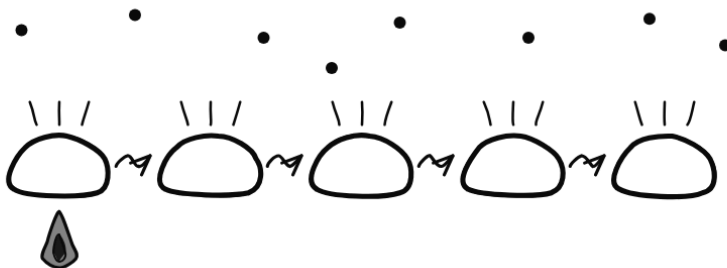


Every Force Turns Into Another

Chemical change in a certain direction takes place not only because of the difference of masses, of the composition of bodies and of the distribution of parts and affinities, or chemical energy, in them, but also under the influence of the conditions in which the substances are placed. For a certain chemical reaction to take place between bodies that are able to react, many conditions are often needed, sometimes very different from the ordinary conditions among which bodies are found in nature. Thus, for example, for charcoal to burn there must be not only the presence of air, and precisely of the oxygen in it, but besides this the charcoal must be red-hot, that is, heated to a

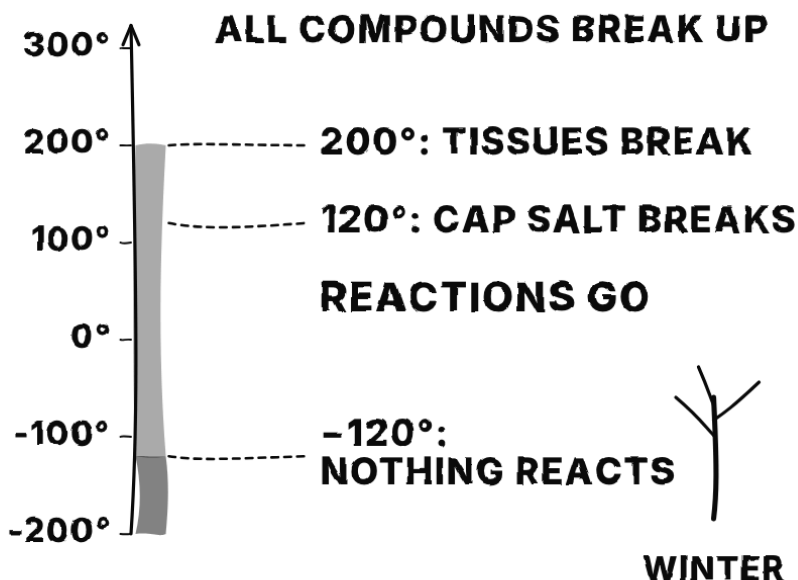
considerable heat. The red-hot part of the charcoal catches fire, that is, combines with the oxygen of the air, and in the process heat is given off, which serves to make other parts of the charcoal red-hot, and these burn only because they have been made red-hot beforehand. Just as the burning of charcoal is conditioned by its being made red-hot, so every chemical reaction goes only under certain physical, mechanical and other conditions. The chief conditions that influence the course of chemical reactions are the following.

OXYGEN OF THE AIR



RED-HOT THE HEAT SPREADS

Charcoal Must Be Red-Hot



A Window of Temperature

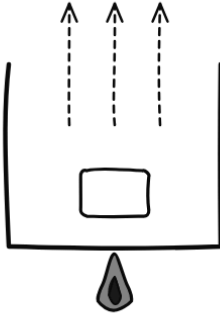
a) The degree of heating. Reactions of combination go only within certain definite limits of temperature, and outside these temperatures they do not take place. One may give as an example not only the fact that burning, as was pointed out above, begins and goes on only on strong heating, but even the fact that the compounds of chlorine or of common salt with water are formed only at temperatures below 0° . At higher temperatures the formation of these compounds does not take place, and the compounds already formed are wholly or partly destroyed into their component parts. In some cases, while a reaction of combination is going on, this can be explained by the fact that one of the reacting bodies then turns from the solid state into the liquid or vaporous one. Turning into a liquid helps the course of the reaction because it helps the full contact of the particles acting on one another.

Another cause to which importance must be ascribed in explaining the influence of heating in starting reactions is that physical cohesion, or the internal bond of similar particles, decreases on heating, and thus the separation of the parts of the bodies taken, and their transformation into new compounds, takes place more easily. In the case where the reaction requires the absorption of heat, as in decomposition, the need for heating is self-evident. On the basis of all the data on the action of high temperature it can now be asserted that all complex bodies decompose under a more or less strong heat. We have already seen examples of such decomposition in describing the decomposition of red mercury oxide into mercury and oxygen and the decomposition of wood under the influence of heat. Many bodies decompose at a slight heat; for example, the fulminating mercury salt that is put into percussion caps, or gun caps, decomposes on heating to just a little above 120° . A multitude of the bodies that make up the tissues of animals and plants decompose already at a temperature of 200° . On the other hand, at very low temperatures no chemical reactions take place at all. We see this in plants, which stop their chemical processes in the cold of winter. Raoul Pictet (1892), using the very low temperatures (down to -200° C) obtained by the boiling of liquefied gases, confirmed that at temperatures below -120° not even such reactions take place as those between sulphuric acid and caustic soda or metallic sodium, and that even the colouring of litmus by acids begins only at temperatures above -80° . Thus every chemical reaction requires certain limits of temperature for its course, and on the sun, where temperatures are very high, or on the moon, where they are very low, a multitude of the chemical transformations we observe on earth undoubtedly cannot take place.

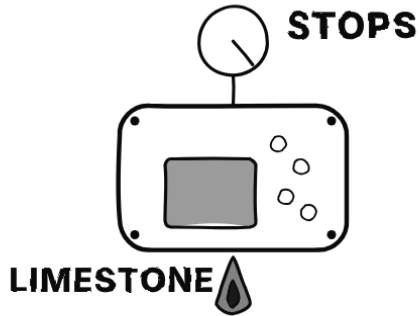
The influence of heating on reversible chemical reactions is especially instructive. If, for example, one heats a complex body that is able to arise back from its products of decomposition, and reaches a certain temperature at which decomposition begins, then for a definite mass of substance enclosed in a definite volume the decomposition does not finish at once, either in time or in quantity. Only a certain share of the substance decomposes, while the other part remains unchanged; if the temperature rises, the quantity of decomposed substance increases, and thereafter to each definite temperature there corresponds, at a given volume, its own ratio between decomposed and untouched substance, until the temperature reaches that at which the complex body breaks up completely. This incomplete decomposition under the influence of temperature is called dissociation. One can distinguish the temperatures of the beginning and the end of dissociation. If at a given temperature dissociation takes place, but one or all of the products of breaking up do not remain in contact with the complex, undecomposed body, then the decomposition will go on to the end. Thus limestone in the heat of a kiln while it is fired decomposes wholly into lime and carbonic acid gas, because the latter can escape. But if a certain mass of the same stone is shut up in a definite volume, for example placed in a gun barrel which is then riveted shut and strongly heated, the carbonic acid gas cannot escape, and then at each temperature higher than the initial dissociation temperature only a certain share of the stone will decompose. The decomposition will stop when the carbonic acid gas given off exerts the greatest dissociation pressure corresponding to the given temperature. If the pressure is increased by adding gas, combination will begin again; if the pressure is decreased, decomposition will go on. Decomposition here is entirely similar to evaporation: if the vapour is not removed, its pressure reaches the

greatest that corresponds to the temperature, and evaporation stops. If more vapour is then added, it will condense into liquid; if some is taken away, that is, if the pressure is lowered while the temperature is kept, evaporation will take place. These notions of dissociation, introduced into science by Henri Sainte-Claire Deville, we shall develop more than once later on. Let us note further that the separated component parts of a substance combine the more easily the nearer their temperature is to the temperature at which dissociation begins; that is, the temperature at which dissociation begins is close to the temperature at which reacting begins. In some cases there exists a perfectly definite temperature of chemical transformation, which can be determined directly (and likened to the temperatures of melting or boiling): above it there takes place, for example, the breaking up of the complex body, and below it its combination, or formation, which can be observed not only with the help of a thermometer but also by the rapid change of volume (with a dilatometer) that sets in at such a transition temperature. Thus natural gypsum, or the calcium sulphate salt with two waters, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, at 107° breaks up completely (in a closed space, otherwise the water will fly off as vapour) into a liquid pulp containing three quarters of the former water in liquid form and the calcium sulphate salt with half a water, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; and at lower temperatures the salt with two waters arises again.

DISSOCIATION

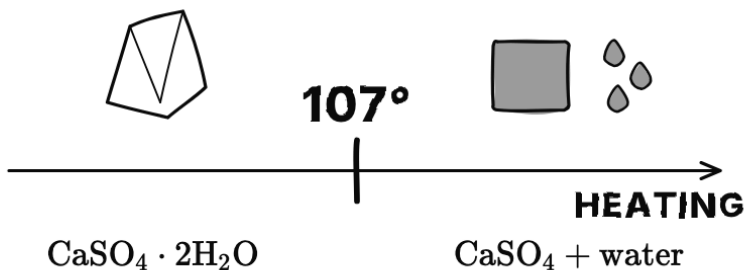


**OPEN KILN: ALL
LIMESTONE → LIME**



**SEALED: ONLY PART
+ GAS → COMBINES AGAIN**

Dissociation in a Closed Barrel



LIKE A MELTING POINT

Gypsum Changes at 107 Degrees

Questions

1. Why does charcoal, once lit, keep burning by itself?
 - a. Because the heat given off by the burning part makes the next parts red-hot, and only red-hot charcoal burns
 - b. Because charcoal burns at any temperature once air is present
 - c. Because the oxygen of the air is heated by the sun
 - d. Because the first spark stores enough heat for all the charcoal

2. Limestone in an open kiln decomposes completely, but sealed in a riveted gun barrel only part of it decomposes. Why?
 - a. Because the gun barrel cannot be heated as strongly as a kiln
 - b. Because in the barrel the carbonic acid gas cannot escape, and decomposition stops when its pressure reaches the greatest value for that temperature
 - c. Because iron reacts with the limestone and protects it
 - d. Because lime is formed only in the presence of fire
3. In the sealed barrel, gas is pumped in so that the pressure rises while the temperature is kept the same. What happens?
 - a. More limestone decomposes
 - b. Nothing changes, since only temperature matters
 - c. Combination begins again: lime and carbonic acid gas re-form limestone
4. What did Pictet's experiments at very low temperatures show?
 - a. That all reactions go faster in the cold
 - b. That litmus changes colour only below minus eighty degrees
 - c. That sulphuric acid freezes sodium solid
 - d. That below about minus a hundred and twenty degrees even vigorous reactions do not take place

Answers

1. **a)** The red-hot part combines with the oxygen of the air and gives off heat, which makes other parts red-hot, and these burn only because they have been made red-hot beforehand.
2. **b)** In the closed barrel the gas cannot escape, so only a share of the stone decomposes; the decomposition stops at the greatest dissociation pressure

for the temperature.

3. c) If the pressure is increased by adding gas, combination will begin again, just as added vapour condenses into liquid.

4. d) Below minus a hundred and twenty degrees not even the reactions of sulphuric acid with caustic soda or sodium take place, so every reaction has its limits of temperature.

Worked examples

Heat measured as work The mechanical equivalent of heat is 425 kilogram-metres of work for one calorie (one kilogram unit of heat). How much mechanical work corresponds to 4 calories?

The equivalent says that one calorie and 425 kilogram-metres of work are the same amount of energy in different forms.

So 4 calories correspond to 4 times as much work.

$$4 \times 425 = 1700.$$

Answer: 1700 kilogram-metres

Practice

1. A machine does 2125 kilogram-metres of work, and all of it turns into heat. How many calories is that, using 425 kilogram-metres to one calorie?

Hint: Divide the work by the work that corresponds to one calorie.

Answer: 5 calories, since $2125 / 425 = 5$.

2. Gypsum, the calcium sulphate salt with two waters, breaks up at 107° in a closed space into the salt with half a water and liquid water. Show that this liquid water is three quarters of the water the gypsum held, and say what happens when it cools below 107° .

Hint: Compare two waters before with half a water kept by the new salt.

Answer: Of the two waters, the new salt keeps half a water, so $2 - \frac{1}{2} = 1\frac{1}{2}$ waters are set free, and $1\frac{1}{2}$ out of 2 is three quarters. Below 107° the salt with two waters forms again, so this is a definite transition temperature, like a melting point.

3. Explain in your own words why dissociation is compared with evaporation.

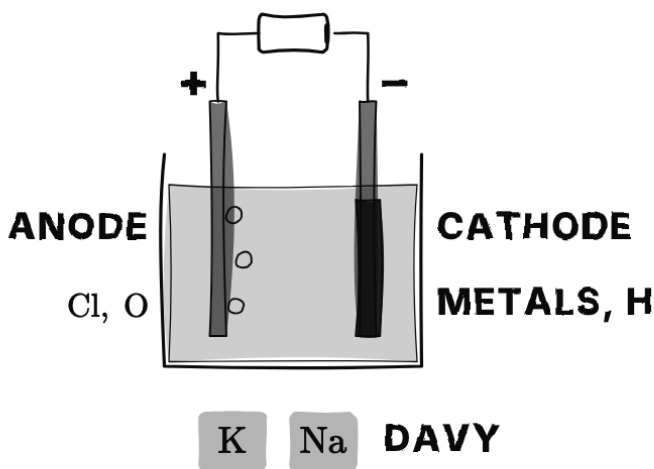
Hint: Think about what happens when the vapour, or the gas, cannot get away.

Answer: In both, if the vapour or gas is not removed, its pressure rises to a greatest value fixed by the temperature and then the process stops. Adding more gas or vapour makes it go back, combining or condensing; taking some away lets the decomposition or evaporation go on.

Introduction

b) The influence of the galvanic current, and of electricity in general, on the course of chemical transformations is very similar to the influence of heat. Most complex bodies that conduct the galvanic current decompose under its action. And near the conditions under which decomposition takes place, combinations usually take place too, and therefore combination often sets in from the action of electricity, exactly as with heating. Electricity must also be regarded as a particular kind of molecular motion, like heat, and everything that relates to the influence of heat relates also to the influences produced by the action of the current; only here the division of a body into its component parts can sometimes be achieved with greater convenience, because it takes place at ordinary temperature. The most stable bodies can be decomposed in this way, and here one notices the important peculiarity that the component parts appear at different poles, or electrodes, through which the current passes into the body. The substances that appear at the positive pole (the anode) are called electronegative, and those that appear (as, for example, metals) at the cathode, that is, at the negative pole, are called electropositive. To the class of the former belong non-metallic bodies, at least in most cases, such as chlorine, oxygen and the like, and also acids and bodies similar to them. At the negative pole, on the other hand, appear metals, hydrogen and products of decomposition similar to it, or ions. The decomposition of complex bodies by means of the galvanic current led in the history of chemistry to very important discoveries. Many simple bodies were obtained in this way. Especially famous is the obtaining of the metals potassium and sodium, whose compounds

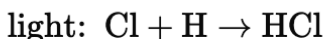
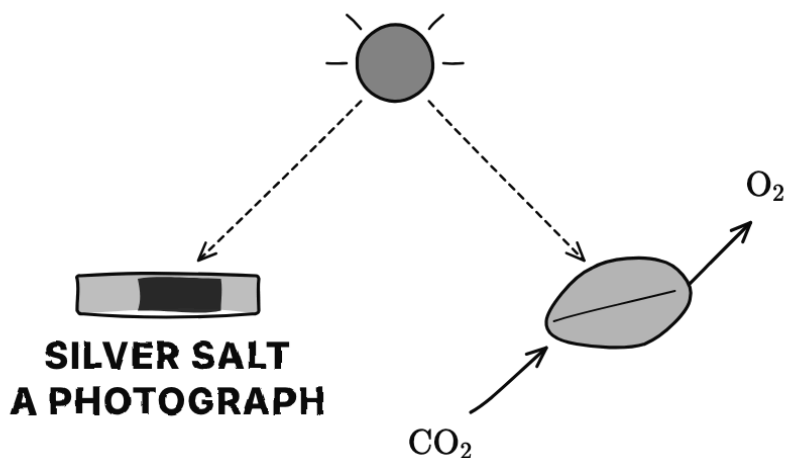
with oxygen Lavoisier and the chemists of his time did not know how to decompose. The Englishman Davy showed that these substances are decomposed by the galvanic current, and at the negative pole he obtained the metals contained in these compounds, namely potassium and sodium. In recent times, when dynamo machines have made it possible to obtain a galvanic current conveniently, by burning fuel or by using water power and other motors, it has become convenient and profitable to apply Davy's method to the factory production of metals, for example sodium from molten NaHO , chlorine from solutions of common salt, and so on.



Splitting by Current

c) Some unstable compounds are also decomposed by the action of light. Photography is based on this property of certain substances (for

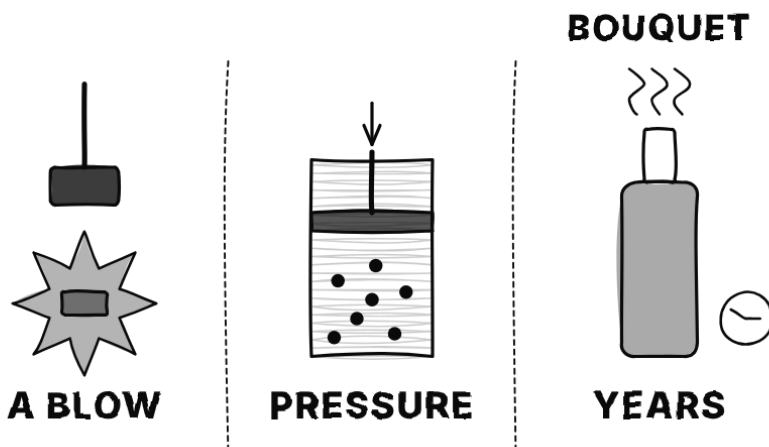
example, salts of silver). The mechanical work of the vibrations that determine the phenomena of light is very small, and therefore only certain bodies, generally unstable ones, can be decomposed by light, at least under ordinary conditions. But there are kinds of chemical phenomena determined by light that form a still unsolved problem of chemistry. These are precisely the phenomena taking place in plants under the influence of light. Here very diverse decompositions and combinations take place, often not yet reproduced by artificial means. Thus, for example, carbonic acid gas, so stable towards the action of the current and of heat, is decomposed in plants under the influence of light, giving off oxygen. Chlorine combines with hydrogen not only under the influence of heat but also under the influence of light, showing that combinations, just like decompositions, can be excited by the action of light.



Light Can Split and Join

d) Mechanical influences, like the influences of the preceding kinds, exert their action both on the course of chemical combinations and on the course of chemical decompositions. Many substances decompose from mere friction or a blow. Such, for example, is the compound called nitrogen iodide, which contains nitrogen, iodine and hydrogen; and such is the fulminating mercury salt, which decomposes from a blow in gun caps (percussion caps). Mechanical friction makes sulphur burn at the expense of the oxygen contained in Berthollet's salt. Pressure also influences both the physical and the chemical state of reacting substances, and together with temperature determines the state of substances; this shows itself especially clearly when a substance is in the elastic gaseous form, since then the volumes change greatly with a change of pressure, and consequently so does

the number of points of meeting of dissimilar substances. Thus compressed hydrogen gas acts more energetically on iodine and on solutions of many salts, under suitable conditions of temperature.



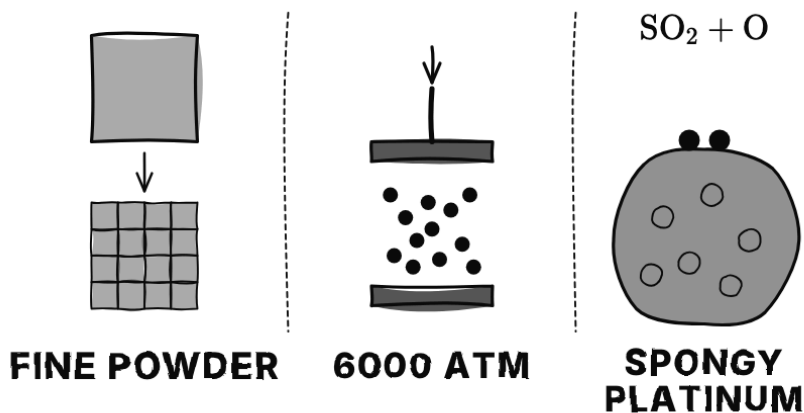
Blows, Pressure and Time

e) The influence of time on the course of reactions shows itself not only in the fact that for bodies to penetrate one another, so that chemical action between them may be possible, mechanical displacement is necessary, which can take place only with a definite speed (thus the burning of a solid substance in air, taking place at its surface, is determined by the renewal of that surface and by the inflow of air, which takes place only with a limited speed); but also in the fact that after full contact the internal displacement that determines chemical reactions requires its own time, or takes place only with a

definite speed. A generally known example is the so-called maturing, or ageing, of grape wine, which helps the appearance in the wine of a particular "bouquet", or aromatic principles. These arise from the acids and the spirit contained separately in fresh (young) wine, which, when the wine is kept, give through their interaction (double decomposition) water and aromatic compound ethers. This reaction, proceeding slowly at ordinary temperature and belonging to the reversible ones (that is, the compound ethers and water are able to give spirit and acid), goes on with a clearly limited speed, the size of which depends on the temperature and other conditions. There are many such slowly proceeding reactions, but most of the sharpest chemical transformations (with which one must become acquainted first of all at the beginning of the study of chemistry) proceed so quickly that time is usually not taken into account in discussing them.

f) Besides the various circumstances set out above, the course of chemical reactions is favoured or hindered by the state of contact in which the acting bodies are found. To increase the number of points of contact means, other things being equal, to increase the intensity of the course of reactions. It is enough to point to a single example: sulphuric acid does not absorb olefiant gas under ordinary conditions of contact, but on prolonged shaking such absorption takes place, because the number of points in contact increases very considerably. When solid bodies are made to act on one another, then for their full and quickest interaction it is necessary to mix them together as finely as possible, turning them into as fine a powder as possible. The Belgian chemist Spring showed that powders of solid bodies that do not react with one another at ordinary temperature can be made to react under increased pressure. Thus at a pressure of 6000 atmospheres sulphur is able to combine with many metals at ordinary

temperature, and the powders of many metals form an alloy at ordinary temperature. It is evident that here one must first of all recognise the increase of the points or planes of contact as the cause of the interaction that sets in, which undoubtedly can take place with solid bodies as with liquid or gaseous ones, because in all states of matter, though in different measure and form, one must recognise the existence of internal motion and the mobility of the particles that make up the bodies themselves. It is very important to pay attention to the fact that the internal motion, or the state of the parts in the particles of bodies, must be different inside a substance and at its surface, because inside a body each particle of the substance is acted on from all sides by other particles like it, while at the surface of bodies it is acted on from one side only. Therefore the state of a substance at its surfaces of contact with other bodies will be more or less changed by them, and may be such as when the temperature is raised. This consideration explains the numerous class of contact chemical reactions, that is, those arising from the presence (contact, catalysis) of certain particular bodies. Porous and powdery bodies especially often act in this way, and among them above all spongy platinum and charcoal. Thus sulphurous gas does not combine directly with oxygen, but in the presence of spongy platinum combination takes place, with the evolution of heat.



More Contact, Faster Change

The general, introductory chemical notions set out above acquire their real meaning only on acquaintance with chemical particulars, to which we shall now pass. Nevertheless it was unavoidable to become acquainted from the very beginning with such all-embracing principles as the laws of the conservation of matter and of forces, because only when they are recognised, and only under their influence, can the examination of particulars be manageable and fruitful.

Questions

1. When a galvanic current decomposes a compound, where do the metals and hydrogen appear?
 - a. At the negative pole, the cathode, which is why they are called electropositive
 - b. At the positive pole, the anode, which is why they are called electronegative
 - c. At both poles equally
 - d. Nowhere: they stay dissolved in the liquid
2. Why can light decompose only certain, generally unstable, bodies under ordinary conditions?
 - a. Because light acts only on silver
 - b. Because the mechanical work of the vibrations of light is very small
 - c. Because light cannot reach the inside of a body
 - d. Because light only causes combinations, not decompositions
3. Sulphuric acid does not absorb olefiant gas when they merely touch, but does after long shaking. Why?
 - a. Because shaking heats the acid
 - b. Because shaking makes the gas heavier
 - c. Because shaking greatly increases the number of points of contact
4. How does the passage explain that spongy platinum makes sulphurous gas combine with oxygen?
 - a. The platinum itself combines with the oxygen and is used up
 - b. The platinum gives off heat of its own
 - c. The platinum supplies the missing sulphur

- d. At a surface each particle is acted on from one side only, so the state of substances touching it is changed, as if the temperature were raised

Answers

1. **a)** Metals, hydrogen and similar products of decomposition appear at the negative pole, and the substances appearing at the cathode are called electropositive.
2. **b)** The mechanical work of the vibrations that determine light is very small, so only unstable bodies can be decomposed by light.
3. **c)** On prolonged shaking the absorption takes place because the number of points in contact increases very considerably.
4. **d)** The state of a substance at its surfaces of contact is changed, and may be such as when the temperature is raised; this explains contact reactions, or catalysis.

Practice

1. Lavoisier could not decompose the compounds of potassium and sodium with oxygen. Explain how Davy did it, and why his method became a factory method later.

Hint: Think about which pole metals appear at, and what made a current cheap to obtain.

Answer: Davy passed a galvanic current through these compounds, and the metals potassium and sodium appeared at the negative pole. Later, dynamo machines driven by fuel or water power made current cheap, so the same method became profitable for producing metals such as sodium, and chlorine from salt solutions.

2. Explain in your own words why young wine develops its bouquet only slowly as it is kept.

Hint: Which substances react, at what temperature, and is the reaction reversible?

Answer: The acids and the spirit in young wine react by double decomposition to give water and aromatic compound ethers. At ordinary temperature this reaction goes on only with a limited speed, and it is reversible, so it takes a long time for the bouquet to develop.

3. Spring made sulphur combine with metals at ordinary temperature. What did he use, and what is the reason the passage gives for the reaction?

Hint: Think of what pressure does to powders that touch.

Answer: He pressed the powders at about 6000 atmospheres. The pressure increases the points or planes of contact between the particles, and since there is internal motion in all states of matter, solids can then react just as liquids and gases do.