

The Principles of Chemistry



Dmitri Mendeleev · 1903

Illustrated audio lectures

Lecturized

The Principles of Chemistry

Illustrated audio lectures

Dmitri Mendeleev · 1903

Retold as illustrated lectures by Lecturized
lecturized.com

From the original: Д. И. Менделеев, Основы химии, 7-е изд. (С.-Петербург, 1903)

Contents

Nothing Is Lost on the Scales

The Scales That Catch a Missing Gas

A White Powder and the Philosopher's Stone

Twelve Days Under a Glass Bell

Every Element Keeps Its Own Account

Seventy-Seven Bricks and the Force That Binds Them

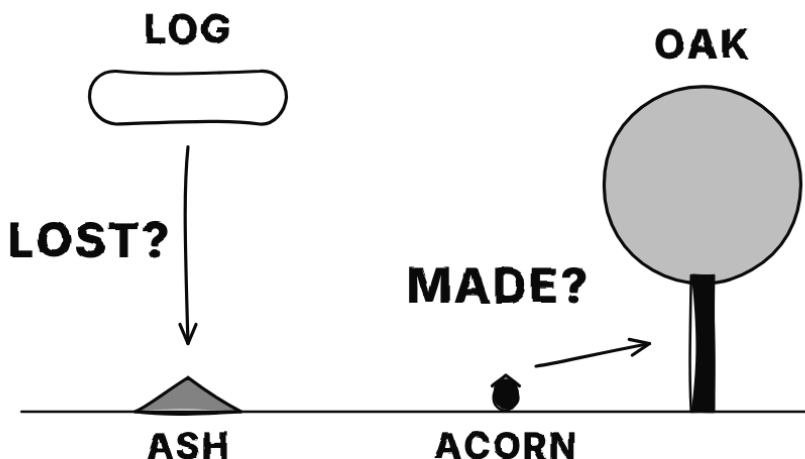
The Hidden Store of Chemical Energy

Heat Opens and Closes the Door

Current, Light, a Blow and a Touch of Platinum

Nothing Is Lost on the Scales

Put a log on a campfire and come back an hour later. Where the heavy log lay, there is a small heap of grey ash and a few black lumps of charcoal. Now picture the opposite scene: a seed that weighs less than a paper clip, and, years later, an oak that weighs as much as a lorry. It looks as if matter can vanish into nothing in the first case and appear out of nothing in the second. Mendeleev opens his great textbook of chemistry by showing why both impressions are wrong, and why getting this right was the moment chemistry became a science.



Lost in fire, made in a tree?

First, what is chemistry about? Mendeleev says that its nearest subject is the study of uniform substances, the ones from which every body in the world is put together, how they turn into one another, and what happens while they do. Such a change is called a reaction. A reaction happens only when the substances touch each other as closely as possible, and it is driven by forces that belong to the tiniest, invisible particles of matter, which he calls molecules. Physics had already given names to gravity, cohesion, heat, light and electricity. Chemistry had to admit something more: hidden forces inside the smallest particles, quiet in ordinary conditions and plainly at work whenever one substance becomes another.

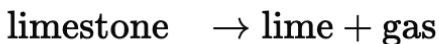
Mendeleev sorts reactions into three main kinds. The first is combination: from two substances one new substance appears, or in general, from a given number of substances, fewer come out. His example can be done on a school bench. Mix iron filings with yellow powdered sulphur. As long as it is only a mixture, a magnet will pull the iron out, and a suitable oily liquid will dissolve the sulphur away. Now heat the mixture. It glows, and what is left is a dark new substance, iron sulphide, in which not even the strongest magnifying glass can find a grain of iron or a speck of sulphur. The two have soaked into each other and can no longer be told apart or separated by hand. Combinations usually give off heat, and ordinary burning is just such a combination: the fuel joins with a part of the air called oxygen, and the result is the gases and vapours of the flame and the smoke. The gas flame on a kitchen stove is a combination of this kind, happening quietly every time you boil water.

COMBINATION



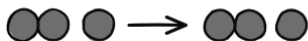
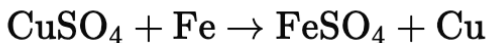
IRON + SULPHUR → IRON SULPHIDE

DECOMPOSITION



THE GAS IS CARBON DIOXIDE

SUBSTITUTION

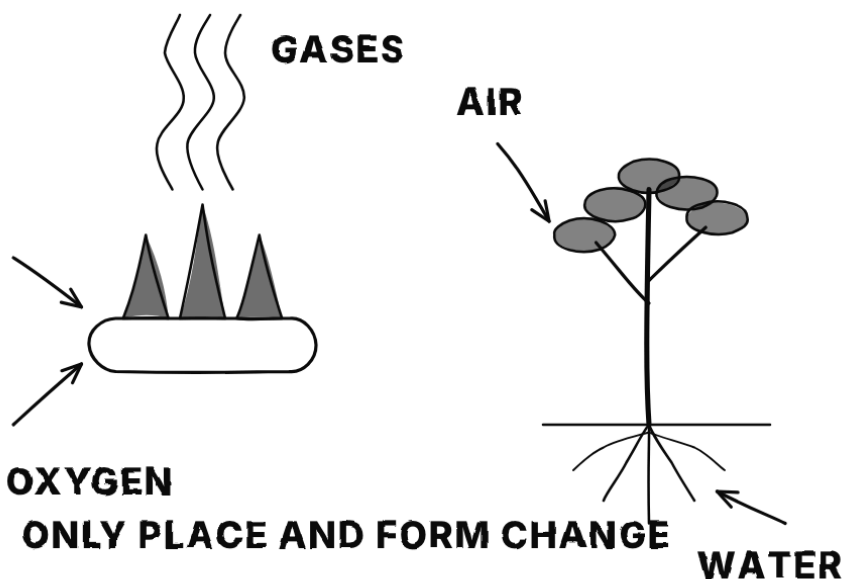


Three kinds of reaction

The second kind is decomposition, the reverse: one substance gives two, or a given number gives more. Heat wood strongly with no air reaching it, and you get a gas that burns, a watery liquid, tar, and charcoal. Factories once made tar, lighting gas and charcoal in exactly this way, on a large scale. Limestone, chalk and marble, when strongly heated, break down too: they leave behind lime and release a special gas, carbon dioxide. The green copper compound found in the mineral malachite does the same thing at a far lower temperature, low enough for thin glass to survive it; we shall come back to it soon. Where combinations usually release heat, decompositions usually swallow it. That is why a lime kiln at a cement factory has to burn fuel all the time: breaking limestone apart costs heat.

The third kind takes as many substances in as it gives out, and can be pictured as a decomposition and a combination happening together. Suppose you start with two bodies and end with two other bodies. Imagine that the first body splits into two pieces, keeps one of them as the first product, and hands the other piece over to the second body, which joins with it to make the second product. Mendeleev calls such reactions displacements; when two substances give two new ones, the reaction is called substitution, or double decomposition. Here is the demonstration. Dissolve blue vitriol, the blue crystals of copper sulphate, in water, and dip an iron nail into the blue solution. After a while the nail is coated in red copper, and the solution has turned into green vitriol, iron sulphate, which differs from the blue salt only in that iron has taken the place of copper. In the same way iron can be coated with copper, and copper with silver, and these reactions are used constantly in practice. Electroplating a cheap fork with a thin skin of silver is a modern cousin of this nail in blue water.

Why did people use chemical changes for thousands of years without having a science of them? Mendeleev gives two reasons. The first is that most changes in nature and in industry are tangled: many combinations, decompositions and substitutions go on at once. The second, and deeper, is that gases take part in very many reactions, above all the air. Only in the sixteenth and seventeenth centuries did people understand that air has weight, and that a gas is a special springy state of matter that spreads out in every direction. Before that, gases slipped through the accounts unnoticed, and so it seemed that matter could be created and destroyed.



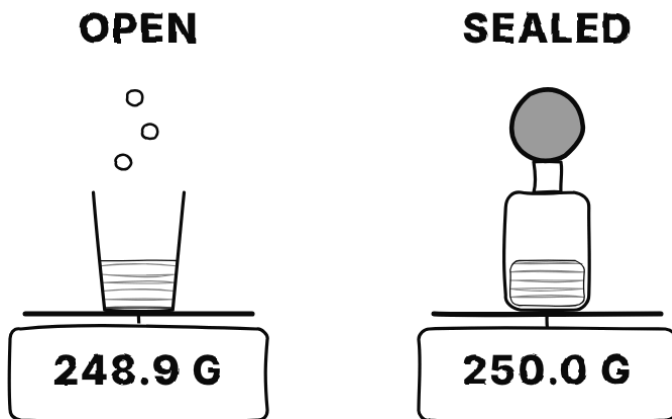
Where the burned log goes

Go back to the burning log. Its substance does not disappear; the chemical change turns it into gases, which leave as smoke. Collect that smoke and you find gases quite unlike air, gases in which a candle goes out and an animal cannot breathe. Weigh them, and they turn out to weigh more than the wood you burned. The extra weight comes from the air: in burning, the parts of the wood join with a part of the air, just as iron gains weight when it rusts. Gunpowder, too, does not vanish when it goes off; it becomes gases and smoke. And the seed does not swell out of itself. It grows because its leaves take in gases from the air and its roots draw up water with dissolved substances, and from these the plant's own chemistry builds its sap and its solid body. Put a plant in a gas without the nourishing part of the air, and it does not grow; it dies. Water that dries off a wet cloth is not lost

either: it comes back as rain, dew and snow, and water that sinks into the ground gathers somewhere and comes out again as a spring. So matter, through every physical and chemical change, only changes its place and its form; it keeps the same amount it had before. In Mendeleev's short phrase, matter is eternal for us.

Try it yourself

Put a glass of water and a small paper bag holding a spoonful of baking soda together on a kitchen scale, and note the reading. Pour a little vinegar into the glass first and weigh again with everything on the pan, then tip the soda in. The mixture fizzes, and if the glass is open, the reading slowly drops as the gas escapes into the room. Repeat the same thing inside a sealed plastic bottle with a balloon stretched over its neck, and the reading does not move at all. The kitchen scale shows what took chemists centuries to see: the missing weight was only the gas you let go.



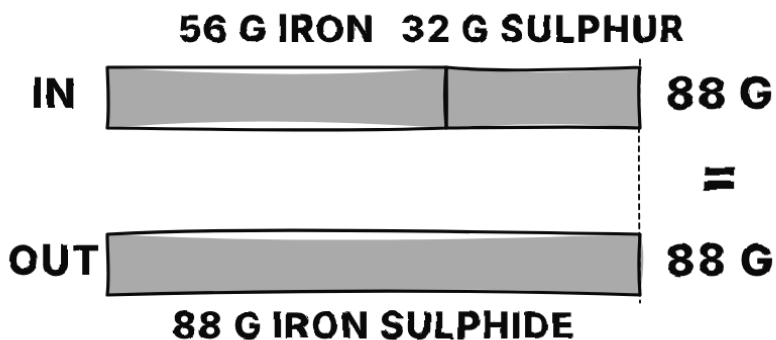
WEIGHT IN = WEIGHT OUT

Open glass, sealed bottle

Some philosophers of ancient Greece, and scientists of the seventeenth century such as Mariotte, already suspected that the total amount of matter stays the same, but none of them stated it clearly or put it to work. The experiments that settled it were made in the second half of the eighteenth century by Antoine Lavoisier, a French academician and also a tax farmer, whom Mendelev calls the founder of modern chemistry. Lavoisier's tool was the balance, the only instrument that tells the quantity of a substance directly and precisely. He weighed every substance he started with, and even the vessels he used, and then weighed everything that came out after the change. Each time he found that the total weight of the products equalled the total weight of the substances he had taken.

That is the law of conservation of matter, and it can be said in several ways: matter is neither created nor destroyed; matter is eternal; the mass, or weight, of matter in nature stays constant. Mendeleev is careful here. He points out that these short phrases contain a guess about all of nature, and that what has actually been seen is longer and more modest. In all our experiments, and in every natural phenomenon studied, nobody has ever found the products weighing more or less than the substances taken, within the precision of the scales. Since weight is proportional to mass, that is, to the amount of matter, nobody has ever seen matter disappear or new matter appear. A modern lab scale reads to a ten-thousandth of a gram, and the law still holds at that precision for every ordinary reaction.

The law is useful as well as true, because it lets you write a balance sheet, an equation, for every reaction. Add up the weights of everything that goes in; add up the weights of everything that comes out; the two sums must be equal. Here is a calculation aloud, using the iron and sulphur from the start. Heat fifty-six grams of iron with thirty-two grams of sulphur, and they make one compound with nothing left over. Fifty-six plus thirty-two is eighty-eight, so the iron sulphide must weigh eighty-eight grams, neither more nor less. And if a burned log seems to weigh less afterwards, the balance sheet tells you at once that something left the room: the missing weight is in the gases of the smoke.



MISSING WEIGHT = GAS

$$56 + 32 = 88$$

Remember

Chemistry studies how uniform substances turn into one another, and every such change, a reaction, needs the closest contact between the particles. Reactions come in three main kinds: combination, where fewer substances come out than went in; decomposition, where more come out; and substitution, where as many come out as went in, as when iron takes the place of copper in blue vitriol. Chemistry came late because reactions are tangled and because gases, which have weight, were left out of the account. Lavoisier, weighing everything before and after, showed that the total weight never changes: matter is neither created nor destroyed. This gives every reaction a balance sheet, where what goes in must weigh exactly as much as what comes out.

Questions

1. Smoke collected from burning wood weighs more than the wood itself. Why?
 - a. Burning creates a little new matter out of the heat of the flame.
 - b. The parts of the wood join with a part of the air, and that air adds its weight.
 - c. Smoke is denser than wood, so the same matter weighs more as smoke.

- d. The ash left behind has passed some of its weight to the smoke.
2. An iron nail is dipped into a blue solution of copper vitriol, and red copper appears on it while the solution turns green. Which kind of reaction is this?
- a. A combination, because the copper joins with the nail.
 - b. A decomposition, because the blue salt falls apart into copper alone.
 - c. A substitution, because iron takes the place of copper and two substances give two new ones.
 - d. No reaction at all, only copper settling out of a mixture.
3. Why did a true science of chemistry arise only after the sixteenth and seventeenth centuries?
- a. Only then did people understand that air and gases have weight and take part in reactions.
 - b. Only then were furnaces hot enough to make reactions happen.
 - c. Only then did people first begin to use chemical changes in their work.
 - d. Only then were molecules seen under a microscope.
4. Before heating, a magnet pulls iron out of an iron and sulphur mixture; after heating, it cannot. What does this show?
- a. The heat has destroyed the iron.
 - b. The iron has become too hot to be magnetic for a while.
 - c. The iron has escaped as a gas while the mixture glowed.

- d. A new substance has formed in which iron and sulphur can no longer be told apart.

Answers

1. **b)** In burning, the wood combines with a part of the air, just as rusting iron does, so the gases carry the weight of the wood plus the weight of the air taken in.
2. **c)** Two substances, iron and blue vitriol, give two new ones, copper and green vitriol, because iron has taken copper's place in the salt.
3. **a)** Before people knew that gases have weight, gases slipped through the accounts unnoticed, so matter seemed to be created and destroyed and no exact account was possible.
4. **d)** The two have combined into iron sulphide, in which neither iron nor sulphur can be found or separated by hand, unlike in the earlier mixture.

Worked examples

Weighing a combination A chemist heats 14 grams of iron filings with 8 grams of sulphur. Both are used up completely and form iron sulphide. How much does the iron sulphide weigh?

By the conservation of matter, the total weight of what comes out equals the total weight of what went in.

What went in is 14 grams of iron and 8 grams of sulphur, together 22 grams.

Nothing else took part and nothing is left over, so the only product carries the whole weight.

So the iron sulphide weighs 22 grams.

Answer: 22 grams

Finding the gas you cannot see A piece of chalk weighing 100 grams is heated strongly until it has all broken down, and the lime left behind weighs 56 grams. How much carbon dioxide gas went off?

Heating chalk is a decomposition: one substance gives lime and the gas carbon dioxide.

By the conservation of matter, the lime and the gas together must weigh as much as the chalk, 100 grams.

The lime is 56 grams, so the gas is what remains: 100 minus 56.

That is 44 grams of carbon dioxide, which escaped unseen into the air.

Answer: 44 grams

Practice

1. An iron nail is left to rust in a closed jar of air. Afterwards the rusty nail weighs more than the clean one did. Does the closed jar with everything in it weigh more, less, or the same as before? Explain.

Hint: Ask where the nail's extra weight came from, and whether that place is inside the jar.

Answer: The same. The nail gained weight by joining with a part of the air, and that air was already inside the jar, so the total weight is unchanged: matter only moved from the air into the rust.

2. In a sealed vessel, 32 grams of a fuel burn completely with oxygen from the air inside, and the gases formed weigh 160 grams in all. How much oxygen did the fuel take from the air?

Hint: What goes in, the fuel and the oxygen, must weigh as much as what comes out.

Answer: 128 grams. The products weigh 160 grams and the fuel was 32 grams, so the oxygen that joined it was 160 minus 32.

3. A small seed grows into a tree hundreds of times heavier. Explain, without calling it creation of matter, where the tree's weight came from.

Hint: Think about what the leaves and the roots take in.

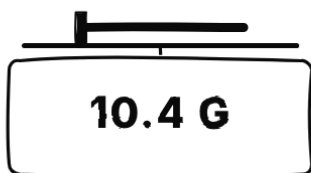
Answer: The tree's matter came from outside: its leaves take in gases from the air and its roots draw up water with dissolved substances, and the plant's chemistry builds its body from them. Nothing was created; matter only changed its place and form.

The Scales That Catch a Missing Gas

Leave a shiny iron nail in a damp place for a week. It turns brown and flaky, and if you had weighed it before, you would find that it is now heavier. Something has been added to it, yet you saw nothing come near it. The balance sheet from the last part, where the weights going in must equal the weights coming out, is about to show us what that something is.

?

$$\sum m_{\text{taken}} = \sum m_{\text{produced}}$$



UNKNOWN → FOUND

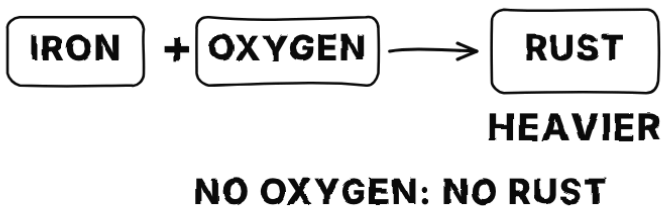
MISMATCH → MISSED

The rusty nail weighs more

Mendeleev puts the law into one line, which in words says this: the weights of all the substances taken, added together, equal the weights

of all the substances produced, added together. That one equality has a practical use. If every weight in it is known except one, the missing one can be worked out. And if a chemist forgets a substance that took part, the two sums will refuse to match, and the mismatch itself gives the omission away. Mendeleev says that anyone starting chemistry must become completely at home with this simple truth, so he gives three examples.

The first is iron. In damp air iron rusts, and heated strongly in air it becomes covered with a scale, an earthy crust much like the iron ores dug from the ground. Weigh the iron before and after, and you find it has gained weight. Lavoisier showed where the gain comes from: from the part of the air called oxygen, the part that keeps a fire burning. The proof is simple: in empty space, or in gases without oxygen such as hydrogen or nitrogen, iron neither rusts nor forms scale. Since the metal grew heavier, the scale must be more complex than the iron, and its forming must be a combination. The rust on an old bicycle chain is heavier than the clean steel it ate, because it has taken oxygen out of the air.

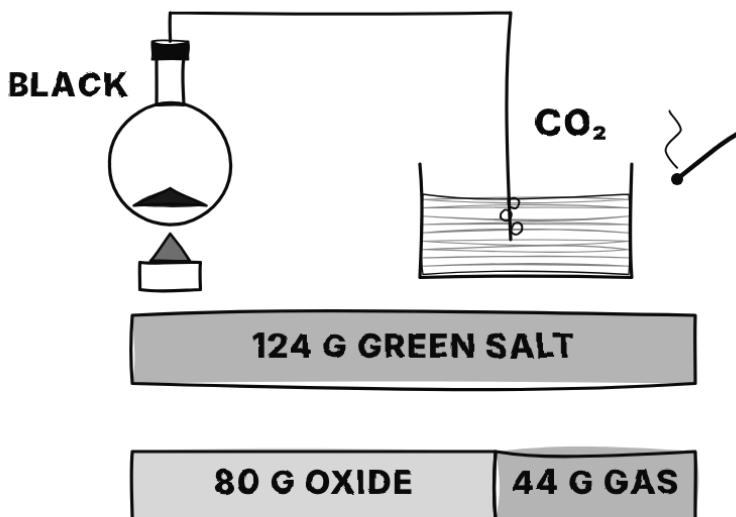


Iron gains, it does not lose

Without the scales, it was easy to get this backwards, and for a long time people did. Before Lavoisier, chemists thought the scale was the simpler body. They imagined that iron contained a mysterious stuff, which they called phlogiston, and that heating drove the phlogiston out and left the earthy scale behind. But if something had left, the scale would weigh less than the iron, and it weighs more. The weighing alone overturned the old idea.

The second example runs the other way. The green powder sold as copper carbonate, and the green stone malachite, used for ornaments and as a copper ore, turn black when heated. The black substance is copper oxide, the same scale that forms on copper heated in air. This time the black residue weighs less than the green salt. So the change is

a decomposition: something has left. Close the vessel with a tight stopper, run a tube from it into water, and as you heat, bubbles of gas come out through the water. Collect that gas and put a burning splinter into it, and the splinter goes out, as if dipped into water; this is carbon dioxide, clear and colourless like air, which is why it was so easy to overlook.

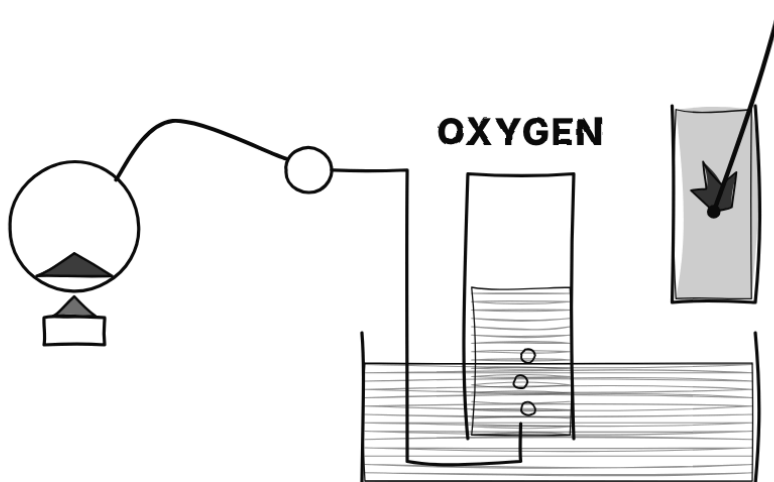


$$124 \text{ g} = 80 \text{ g} + 44 \text{ g}$$

Here is the calculation aloud. Suppose you heat one hundred and twenty-four grams of pure copper carbonate, and eighty grams of black copper oxide remain. The balance sheet says the oxide and the gas together must make up one hundred and twenty-four grams. So the gas must weigh one hundred and twenty-four minus eighty, which is forty-four grams. Mendeleev says exactly this can be checked: weigh

the gas as well, and the weights of the black oxide and the carbon dioxide add up to the weight of the green salt. On a lab scale reading to a hundredth of a gram, the forty-four grams of an invisible gas show up as plainly as the eighty grams of black powder.

The third example is the one Mendeleev calls especially important for the history of chemistry. Heat mercury in air and it slowly turns into a red powder, the red oxide of mercury. Put this red powder into a glass retort, a round flask with a long bent neck. The neck is pushed through a tight cork into a small glass bulb, and from the bulb a tube bends down into a basin of water. Any gas that forms has no other way out than through the tube, so you see it as bubbles in the basin.



Catching the gas under water

To catch the gas, a tall glass cylinder is filled to the brim with water, closed, turned upside down, and opened under the water. The water stays up inside it, held by the pressure of the air on the basin. Set the cylinder's mouth over the end of the tube, and the bubbles rise into it and push the water down. When you heat the retort, first comes ordinary air, expanding from the heat; then comes a different gas. Close the cylinder under water, lift it out, turn it mouth up, and lower in a splinter that is only glowing. In ordinary air such a splinter dies by itself; in this gas it bursts into a bright flame. This is oxygen, a gas that keeps burning going far more strongly than air does.

Try it yourself

Blow out a wooden match and, while the tip is still glowing, hold it over the bubbles of a fresh glass of hydrogen peroxide from the pharmacy with a pinch of dried yeast stirred in. The foam gives off oxygen, and if the glow is close enough, it brightens or even flares up again. This is the same test Mendelev describes, done with a kitchen glass instead of a retort.

At the same time, a shining film and little droplets of liquid metal gather on the cool parts of the retort and in the bulb: mercury vapour condensing. So the red oxide gives two bodies, mercury and oxygen; one has become two, which makes it a decomposition. Again the weights account for each other. Say you heat twenty-one point seven grams of the red oxide and collect twenty point one grams of mercury; then the oxygen that went into the cylinder must weigh one point six grams.



BEFORE

21.7 G RED OXIDE



1.6 G OXYGEN



AFTER

20.1 G MERCURY

THE GAS OF AIR AND FIRE

$$21.7 \text{ g} = 20.1 \text{ g} + 1.6 \text{ g}$$

People before Lavoisier could already collect gases, but he was the one who showed what part they play. The oxygen set free from the red powder is the very gas found in air, the gas that animals breathe, that things burn in, and that turns metals into rust and scale, the earthy substances, like ores, from which metals are won. That is why this small experiment with red powder changed the whole of chemistry.

Remember

The balance sheet of a reaction lets you find one unknown weight from all the others, and it warns you at once when a substance has been left out. Iron grows heavier when it rusts, because it combines with oxygen from the air; the old idea of phlogiston escaping was wrong, as the weighing shows. Green copper carbonate grows lighter on heating, because it decomposes into black copper oxide and carbon dioxide, and the two weigh exactly what the salt did. Red mercury oxide, heated, splits into mercury and oxygen, the gas that makes a glowing splinter blaze up. That oxygen is the same gas that is in the air we breathe and in every fire.

Questions

1. Iron heated in air becomes covered with scale and gets heavier. What does the weighing tell us about the scale?
 - a. It is simpler than iron, because something has been driven out of the metal.
 - b. It is more complex than iron, because the metal has combined with something from the air.
 - c. It is the same substance as iron, only in another form.
 - d. It is ash from impurities that burned away in the iron.
2. Why did the phlogiston idea fail once careful weighing began?

- a. Phlogiston was found to be a gas, so it could not be inside a metal.
 - b. Nobody managed to collect phlogiston in a cylinder over water.
 - c. If phlogiston left the iron, the scale would weigh less, but it weighs more.
 - d. Lavoisier showed that iron never forms scale at all when heated.
3. Green copper carbonate turns into black copper oxide that weighs less than the green salt. What should a chemist conclude first?
- a. Some substance has left the salt, most likely a gas that cannot be seen.
 - b. Part of the matter of the salt has been destroyed by the heat.
 - c. The black oxide is denser, so it weighs less for the same amount.
 - d. The salt has combined with oxygen from the air.
4. How can you tell the gas from red mercury oxide apart from ordinary air?
- a. It puts a burning splinter out, as if it were dipped in water.
 - b. It is coloured, while air is colourless.
 - c. It stays in the cylinder even when the cylinder is opened mouth down.
 - d. A merely glowing splinter bursts into a bright flame in it.

Answers

1. **b)** The metal grew heavier, so something was added: the scale is iron combined with oxygen from the air, a combination and not a loss.
2. **c)** Something leaving would make the scale lighter than the iron; the scale is heavier, so the weighing overturned the old idea.
3. **a)** Since matter is neither lost nor made, a loss of weight means something has gone out: here, colourless carbon dioxide.
4. **d)** In ordinary air a glowing splinter dies by itself; in oxygen it flares up, because oxygen keeps burning going far more strongly than air.

Worked examples

The gas from green copper salt 124 grams of pure copper carbonate are heated until it has all turned black, and 80 grams of black copper oxide remain. How much carbon dioxide was given off?

Heating the green salt is a decomposition into black copper oxide and carbon dioxide.

By the balance sheet, the oxide and the gas together weigh as much as the salt taken, 124 grams.

The oxide weighs 80 grams, so the gas is the difference, 124 minus 80.

That gives 44 grams of carbon dioxide, which left unseen through the tube.

Answer: 44 grams

The oxygen from red mercury oxide 21.7 grams of red mercury oxide are heated until it has all decomposed, and 20.1 grams of mercury are collected. How much oxygen came off?

The red oxide decomposes into two bodies only, mercury and oxygen.

So mercury and oxygen together weigh what the oxide weighed, 21.7 grams.

The mercury is 20.1 grams, so the oxygen is 21.7 minus 20.1.

That is 1.6 grams of oxygen.

Answer: 1.6 grams

Practice

1. A strip of copper weighing 64 grams is heated in air until it has all turned into black copper oxide, which weighs 80 grams. How much of the air's oxygen did the copper take up?

Hint: Copper and oxygen go in, only copper oxide comes out.

Answer: 16 grams. The oxide weighs 80 grams and the copper was 64 grams, so 80 minus 64 grams of oxygen joined it.

2. A student heats some green copper carbonate in an open dish and weighs only the dish before and after. The weights do not match, and they conclude that matter was destroyed. What did they overlook, and how could they check?

Hint: Think of what came out of the salt that the eye cannot see.

Answer: They overlooked the colourless carbon dioxide that escaped. Heating in a stoppered vessel with a tube into water would show the gas as bubbles, and weighing the collected gas would make the two sides of the balance sheet equal.

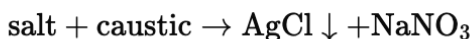
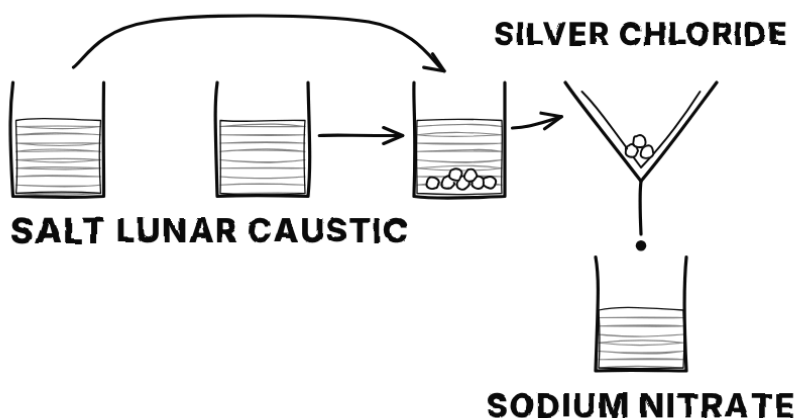
3. Iron is heated in a vessel filled with nitrogen instead of air, and it gains no weight and forms no scale. What does this tell you about where the extra weight of scale comes from?

Hint: Compare with what happens in ordinary air.

Answer: The extra weight must come from the oxygen of the air: in a gas without oxygen, such as nitrogen, iron neither rusts nor forms scale, so without oxygen nothing is added.

A White Powder and the Philosopher's Stone

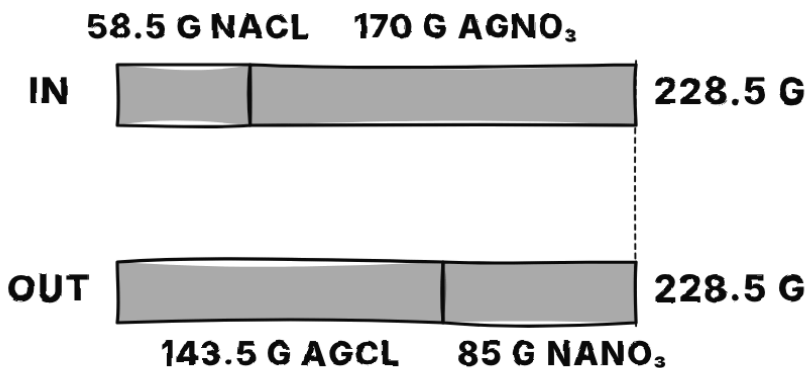
Take two glasses of water that look exactly alike, both perfectly clear. In one, table salt has been dissolved; in the other, lunar caustic, the silver salt that doctors once used to cauterise wounds. Pour one glass into the other. At once the liquid turns milky, and a heavy white powder begins to sink to the bottom. Two clear liquids have made something solid, and Mendeleev uses this little scene for his fourth example of the balance sheet.



Two clear liquids, one white powder

The white powder can be separated by filtering. Take a round sheet of unsized paper, fold it in half and in half again, open it into a cone, and set the cone inside a glass funnel. Pour the cloudy liquid in: the clear solution runs through the paper, and the powder stays behind on it. Dried, the powder turns out to be a quite new substance, silver chloride, and the first sign is that it will not dissolve in water, while both salts we started with did. Now boil the clear liquid that came through until it is dry. It leaves another new salt, soluble in water like the first two, yet different from both: sodium nitrate. A coffee filter in your kitchen works the same way, letting the liquid through and keeping the grounds.

So two soluble substances went in, and through substitution two new ones came out, one that sinks and one that stays dissolved. The water itself did not take part; it only made the two salts liquid and mobile, so that their particles could meet. And now the weighing. Mendeleev gives the numbers: about fifty-eight and a half grams of salt with one hundred and seventy grams of lunar caustic. Together that is two hundred and twenty-eight and a half grams going in. Out come one hundred and forty-three and a half grams of silver chloride and eighty-five grams of sodium nitrate. One hundred and forty-three and a half plus eighty-five is, again, two hundred and twenty-eight and a half grams. The two sides of the balance sheet agree to the half gram, as the law of conservation of matter demands.



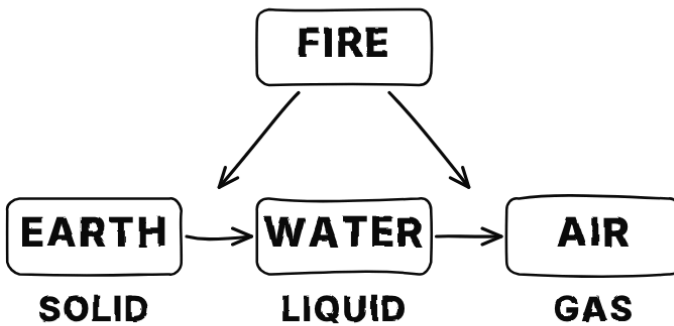
228.5 g in, 228.5 g out

Try it yourself

Dissolve a spoonful of Epsom salt in one glass of warm water and a spoonful of washing soda in another, then pour them together. The clear liquids turn cloudy white at once, because a new substance forms that does not dissolve. Pour the mixture through a coffee filter, and the white solid stays on the paper while clear liquid runs through. It is Mendeleev's salt-and-silver experiment with things from a supermarket shelf.

Once you know that the quantity of matter never changes, a second question arises at once, and Mendeleev calls it the second most

essential question of chemistry. Is there a limit to how substances can turn into one another? Could any substance, in principle, be turned into an equal amount of any other? Or is the circle of possible changes closed? This is a question about the quality of matter, not its quantity, and it is much harder.



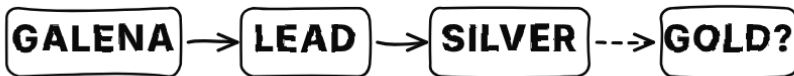
The four old elements

Ordinary experience points both ways. On one side, plants build all their varied substances out of air and soil, and iron can be made into ink and into the deep blue paint called Prussian blue, so it seems the changes have no end. On the other side, everyday experience says you cannot make food out of a stone, or gold out of copper. Only careful study could settle it, and people have answered it differently over the centuries.

The oldest widespread answer was that everything visible is made of four elements: air, water, earth and fire. The idea came from Asia to the Greeks, and Empedocles, who lived about four hundred and sixty years before Christ, set it out most fully. It was not drawn from exact research. It seems to rest on telling gases, like air, from liquids, like water, and solids, like earth, and on noticing that fire, that is, heat, changes them.

Arab scholars were the first to take the question to experiment, and through Spain they brought the love of such inquiry into Europe. From then on there were many followers of this science, thought of as secret, and called alchemy. The alchemists had no firm law to start from, and their great service was that they made a huge number of experiments and discovered many new transformations. Their own answer to the question was that change has no limit: they searched for the philosopher's stone, which would turn anything into gold and diamonds and even make an old body young again.

ALCHEMY



The silver was already there

Mendeleev insists that this was not pure fantasy; the first experiments could honestly lead there. The alchemists took a shiny metallic stone called galena and got lead from it: from a useless stone, a soft and useful metal. Then from that lead they got silver, more precious still. It seemed natural to think that a chain of such steps would ennoble metals further, and having got silver from lead, they set their hearts on getting gold as well.

What they lacked was the scales. Had they weighed, they would have found that the lead weighs much less than the galena it came from, and that the silver is a tiny amount next to the lead used. Had they studied the process closely, they would have seen that lead does not turn into silver at all. Lead found in nature simply contains a little

silver, and once that silver is taken out, no further treatment will give any more. To this day, Mendeleev notes, most of the world's silver is won from natural lead ores in exactly this way. It is like finding a few coins in an old armchair: the chair did not make them, and shaking it again gives you nothing.

The alchemists could never fully succeed, because they did not ask simple, clear questions whose answers would let them move on. So they found no exact law at all. But they left chemistry a rich inheritance of new experimental facts.

Remember

Mixing solutions of table salt and lunar caustic makes two new substances by substitution: insoluble silver chloride, caught on a filter, and soluble sodium nitrate. The weights agree exactly: fifty-eight and a half plus one hundred and seventy grams go in, and one hundred and forty-three and a half plus eighty-five grams come out, two hundred and twenty-eight and a half on each side. After the question of quantity comes the harder question of quality: is there a limit to what a substance can be turned into? The alchemists believed there was none and hunted for the philosopher's stone, misled because they hardly ever weighed. The silver they drew from lead had been in the lead all along; they found no law, yet left chemistry a wealth of experiments.

Questions

1. After mixing salt and lunar caustic solutions, how do we know the white powder on the filter is a new substance?
 - a. It is heavier than both salts together.
 - b. It will not dissolve in water, while both salts we started with did.
 - c. It is white, and lunar caustic is not.
 - d. It forms only when the water is boiled away.
2. What part does the water play in the salt and lunar caustic reaction?
 - a. It only makes the salts liquid and mobile so that their particles can meet.
 - b. It combines with the salt to make silver chloride.
 - c. It is used up and turns into sodium nitrate.
 - d. It adds its weight to the white powder.
3. Why might early experiments honestly lead someone to believe that lead can become silver?
 - a. Because silver and lead have the same colour.
 - b. Because lead slowly turns into silver if it is left in the air.
 - c. Because silver could be drawn out of lead, and without weighing it looked like a transformation.
 - d. Because galena is made of silver and gold.
4. What would weighing have shown the alchemists about their lead and silver?
 - a. That the silver weighed more than the lead used.
 - b. That lead and silver always weigh the same.
 - c. That the lead gained weight as it gave up silver.

- d. That the silver was tiny next to the lead, and that no more could be got once it was taken out.

Answers

1. **b)** Both starting salts dissolve in water; the powder does not, so it must be a quite different substance, silver chloride.
2. **a)** The water did not take part; it only brought the two salts into a liquid, mobile state where they could react.
3. **c)** The alchemists saw silver come out of lead, and since they hardly weighed, they could not see that it was only a small amount already contained in the lead.
4. **d)** The silver was a tiny part of the lead, already there; once removed, no treatment gives any more, so lead does not turn into silver.

Worked examples

Checking Mendeleev's balance sheet About $58\frac{1}{2}$ grams of table salt and 170 grams of lunar caustic react, giving $143\frac{1}{2}$ grams of silver chloride and 85 grams of sodium nitrate. Do the weights obey the conservation of matter?

Add the weights going in: $58\frac{1}{2}$ plus 170 is $228\frac{1}{2}$ grams.

Add the weights coming out: $143\frac{1}{2}$ plus 85 is $228\frac{1}{2}$ grams.

Leave the water out of both sides, because it only helped the salts meet and was not used up.

The two sides are equal, as the conservation of matter demands.

Answer: Yes: $228\frac{1}{2}$ grams on each side.

Practice

1. A student mixes $58\frac{1}{2}$ grams of table salt with 170 grams of lunar caustic in water and filters off $143\frac{1}{2}$ grams of dry silver chloride. How much sodium nitrate should they get when they boil the filtered liquid dry?

Hint: What goes in must weigh the same as what comes out.

Answer: 85 grams. $58\frac{1}{2}$ plus 170 is $228\frac{1}{2}$ grams going in, and $228\frac{1}{2}$ minus $143\frac{1}{2}$ grams of silver chloride leaves 85 grams for the sodium nitrate.

2. Explain the difference between the question of quantity and the question of quality in chemistry.

Hint: One is about how much matter there is, the other about what it can become.

Answer: The question of quantity asks whether the amount of matter changes in a reaction, and the scales answer it: it does not. The question of quality asks whether there is a limit to what a substance can be turned into; it is harder, because everyday experience points both ways.

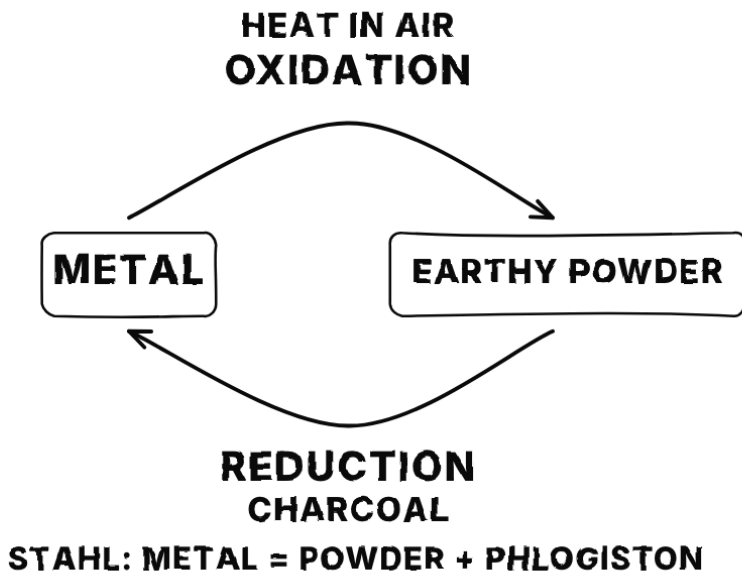
3. Why could the alchemists never fully succeed, according to Mendeleev, even though they made many discoveries?

Hint: Think about the kind of questions they asked, and about weighing.

Answer: They had no firm law to start from, rarely weighed, and did not ask simple, clear questions whose answers would let them move on. So they found no exact law, although they left chemistry a wealth of experimental facts.

Twelve Days Under a Glass Bell

Heat a strip of lead or tin in an open flame, and its bright surface goes dull and crumbles into a grey or yellow powder. Now heat that powder with charcoal, and beads of shining metal appear again. Alchemists did this a thousand times, and so did every smelter of ore. Mendeleev says that because the alchemists studied metals above all, chemistry for a long time was mostly the chemistry of metals. The two changes we just watched were to lead to its most important laws.



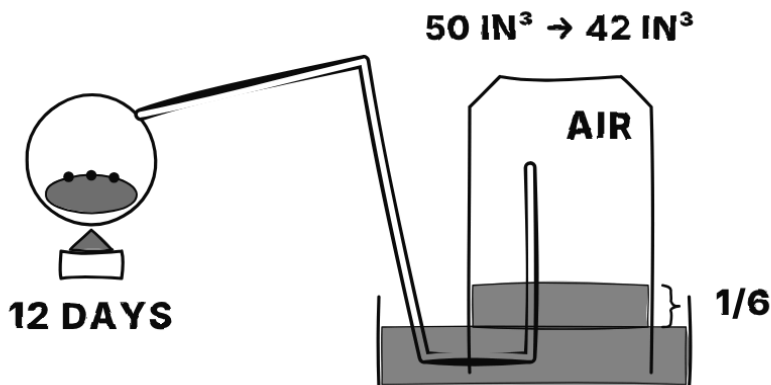
Oxidation and reduction

The first change, a metal rusting or more generally passing from its shining state into an earthy powder, is called oxidation. The reverse, getting the metal back out of the earthy powder, is called reduction. Iron, lead and tin all oxidise simply by being heated in air, and they are reduced again by heating with charcoal. Many ores in the ground are exactly such oxidised metals, and tin, iron and copper are won from them, as from rust or scale, by heating with charcoal. A modern blast furnace still does this on a giant scale: iron ore and coke go in at the top, and molten iron runs out at the bottom.

The first theory to explain both changes came from Becher and above all from Stahl, physician to the King of Prussia, in his book of seventeen twenty-three. Every body, Stahl said, consists of a weightless fiery matter called phlogiston, together with some other element proper to that body. The more easily a body burns or rusts, the more phlogiston it holds, and charcoal holds a great deal. When a body rusts or burns, phlogiston leaves it; when it is reduced, phlogiston comes back in. Charcoal reduces an ore because it is rich in phlogiston and gives some of it to the ore. So for Stahl a metal was a compound, earthy powder plus phlogiston, and the theory was so simple that it found a great many followers.

Lavoisier, with his scales, showed that every rusting, oxidation and burning makes the body heavier, at the expense of the air. He took the natural view that the heavier body is the more complex one. To decide between the two views, he made a famous experiment in seventeen seventy-four.

AIR LOST = MERCURY GAINED



50 cubic inches become 42

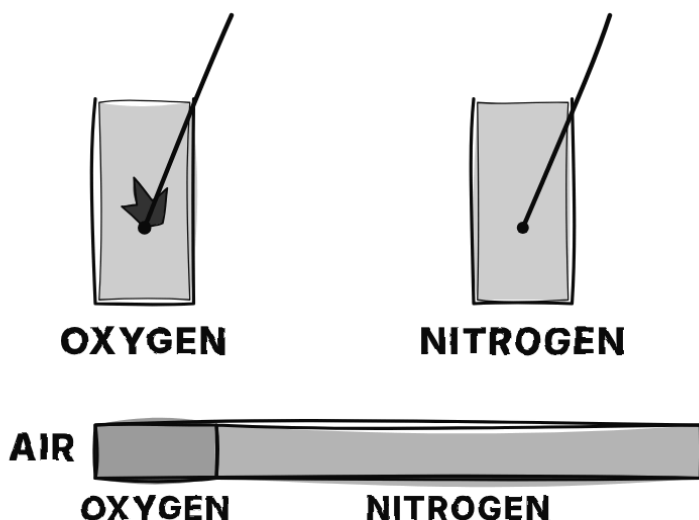
He poured four ounces of pure mercury into a glass retort whose long neck bent down and then up, ending inside a dish that was also filled with mercury. Over the end of the neck stood a glass bell, so that a fixed amount of air was shut off from the room, partly in the retort and partly under the bell. Before starting, he measured the mercury and, very carefully, the volume of that trapped air. For this he had to know the whole capacity of the retort, the volume of mercury poured in, the volume of the bell up to the level of the air, and the temperature and pressure at the moment of measuring. Why such care about the air? Because the two theories made opposite predictions. If Stahl was right, phlogiston would leave the mercury and go into the air, and the air should not shrink. If Lavoisier was

right, the mercury would take up part of the air, and the air should shrink.

For twelve days Lavoisier kept the retort hot, close to the boiling point of mercury. The surface became covered with many little red scales: the mercury was oxidising into the red mercury oxide we met earlier. After twelve days he let everything cool and measured the air again. Of fifty cubic inches of air, only forty-two were left. Here is that result aloud: fifty minus forty-two is eight cubic inches gone, and eight out of fifty is sixteen out of a hundred, about one sixth of the air. The air had shrunk, and that refuted the German chemist's view. More than that, the weight of the air had gone down by exactly as much as the weight of the mercury had gone up. So that part of the air had not been destroyed; it had joined the mercury.

Try it yourself

Wet a pad of steel wool, push it into the bottom of a tall narrow glass, and stand the glass upside down in a saucer of water. Mark the water level inside the glass and look again after a few days. The steel wool has rusted, and the water has risen inside the glass, by roughly a fifth of the air space, then stopped. It is Lavoisier's bell in a kitchen: the rusting iron has taken the oxygen out of the trapped air, and the rest of the air does not rust it any further.

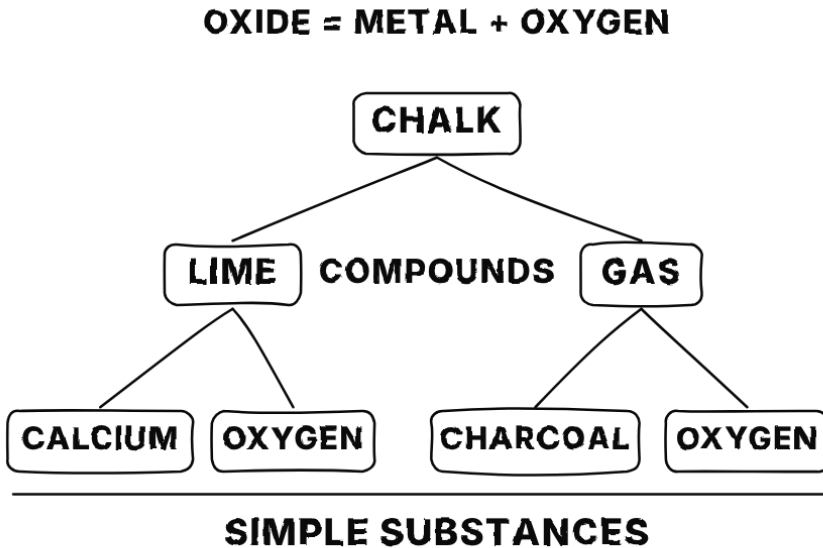


Air is two gases

The part of the air that joined the mercury can be driven out of the red oxide again, as we saw, and it is unlike air: it is oxygen. The part left behind under the bell did not oxidise metals at all and could support neither burning nor breathing. A burning splinter, Lavoisier wrote in his report, "goes out in it as if it were plunged into water". That gas is called nitrogen. So air is not a simple body but consists of two gases, oxygen and nitrogen, and the old view that air is an element is wrong. Mix oxygen with nitrogen again, and you get the same air as before.

Now the whole story turns the right way round. In burning and in the oxidation of metals, the oxygen of the air is taken up. The earthy powders made by oxidising metals are bodies composed of metal and oxygen. And direct experiment showed that when charcoal reduces an

oxide, the oxygen in the oxide passes to the charcoal and makes the same gas that charcoal makes when it burns in air. So that gas too is a compound, of charcoal and oxygen, just as the oxides are compounds of metals and oxygen.



Taking compounds apart

Many examples of combination and decomposition show that most of the bodies around us are compounds made of several others. Heat chalk, as we heated the green copper salt, and you get lime and the same gas that burning charcoal gives. Bring lime together with that gas and some water at ordinary temperature, and you get back a chalk-like substance, so chalk is a compound. But its parts are compounds too: the gas is charcoal plus oxygen, and lime comes from the oxidation of a special metal called calcium. Taking things apart in

this way, one comes in the end to substances that no means can split into others, and that cannot be made from anything. They can only combine with one another or act on other bodies, and they are called simple substances. So all uniform substances fall into two kinds, simple and compound, a division science has kept since Lavoisier.

There are very few simple substances compared with the compounds they form. About seventy-five were known with certainty in Mendeleev's time; some are rare or found only in small amounts. The simple substances whose compounds we meet in daily life number no more than twenty-five. A kitchen holds hundreds of different things, yet most of them are built from just a handful of simple substances, such as carbon, hydrogen, oxygen, sodium and chlorine.

Remember

Oxidation turns a shining metal into an earthy powder; reduction, by heating with charcoal, brings the metal back, and ores are such oxidised metals. Stahl explained both with an imagined weightless phlogiston leaving or entering the metal. Lavoisier heated mercury under a bell of air for twelve days: fifty cubic inches shrank to forty-two, and the air lost exactly the weight the mercury gained. Air is oxygen, which joins metals and keeps fires and breathing going, mixed with nitrogen, which does neither; oxides are metal plus oxygen. Taking compounds apart, we reach simple substances, which cannot be split or made, about seventy-five of them, of which some twenty-five meet us every day.

Questions

1. Why did Lavoisier take such care to measure the trapped air before and after heating the mercury?
 - a. Because the two theories predicted opposite things for the air: unchanged for Stahl, shrinking for Lavoisier.
 - b. Because mercury vapour is poisonous and had to be kept in check.
 - c. Because he wanted to know how hot the retort became.
 - d. Because the air was needed to keep the mercury from boiling.
2. According to Stahl, why does heating an ore with charcoal give back the metal?
 - a. Because charcoal takes oxygen out of the ore.
 - b. Because the heat alone drives the earthiness out of the ore.
 - c. Because charcoal is rich in phlogiston and gives some of it to the ore.
 - d. Because charcoal melts and mixes with the ore.
3. What did the gas left under Lavoisier's bell show about air?
 - a. That air is a single simple substance after all.
 - b. That air is a mixture of two gases, one that joins metals and one that supports neither burning nor breathing.
 - c. That air turns into mercury when heated long enough.
 - d. That air contains phlogiston released from the mercury.

4. How do we know that chalk is a compound and not a simple substance?
- a. Because it is white and soft.
 - b. Because it dissolves completely in water.
 - c. Because it is found everywhere in the ground.
 - d. Because heating splits it into lime and a gas, and these can be joined back into a chalk-like substance.

Answers

1. **a)** If phlogiston left the mercury, the air would not shrink; if the mercury took up part of the air, it would. Only a careful measurement of the air could decide.
2. **c)** For Stahl a metal was earthy powder plus phlogiston, so charcoal, full of phlogiston, restored the metal by handing phlogiston over.
3. **b)** The part that joined the mercury was oxygen; the leftover part, nitrogen, put out a flame. So air is oxygen and nitrogen, not an element.
4. **d)** A simple substance can be neither split nor made; chalk can be split into lime and a gas and remade from them, so it is a compound.

Worked examples

How much of the air joined the mercury In Lavoisier's experiment, 50 cubic inches of air were shut in with the mercury, and after twelve days of heating only 42 cubic inches were left. What share of the air did the mercury take up?

The air lost is the difference between before and after: 50 minus 42 is 8 cubic inches.

To find the share, compare the loss with the whole: 8 out of 50.

8 out of 50 is the same as 16 out of 100, so sixteen per cent.

That is about one sixth of the trapped air, the part that combined with the mercury as oxygen.

Answer: 8 cubic inches, about one sixth (16 per cent) of the air.

Practice

1. In Lavoisier's experiment, the air under the bell lost weight while the mercury gained weight. If the mercury gained 1.2 grams, how much weight did the air lose?

Hint: Nothing is made or lost: where did the mercury's extra weight come from?

Answer: 1.2 grams. The part of the air that disappeared had joined the mercury, so the air lost exactly as much as the mercury gained.

2. Explain why the shrinking of the air refuted Stahl's theory.

Hint: What did Stahl say leaves the metal when it oxidises, and where would it go?

Answer: Stahl held that phlogiston leaves the metal and goes into the air when it oxidises, so the air should not shrink. The air did shrink, by as much weight as the mercury gained, so something went from the air into the metal, not the other way round.

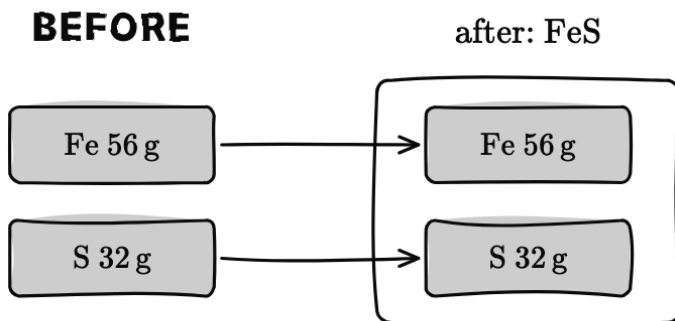
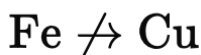
3. When an iron ore is reduced with charcoal, a gas is given off. What is this gas made of, and what does that tell us about the ore?

Hint: Where does the oxygen of the ore go?

Answer: The oxygen of the ore passes to the charcoal and forms the same gas that burning charcoal gives, a compound of charcoal and oxygen. So the ore was iron combined with oxygen, and reduction takes the oxygen away.

Every Element Keeps Its Own Account

Imagine trying to turn a lump of iron into a lump of copper. You may melt it, dissolve it in acid, rust it, reduce it again with charcoal, pass it through a hundred compounds. At the end, however clever the route, what you get back is iron, and exactly as much iron as you started with. Mendeleev's next step is to say why this is so, and what it means for every chemical change.



$$\text{Fe} : 56 = 56$$

$$\text{S} : 32 = 32$$

Each simple substance balances

Simple substances, he says, are not able to turn into one another; at least, not one case of such a change has ever been noticed. So today it

is impossible to turn one metal into another. In spite of a mass of effort, not one fact has turned up to suggest that well-established simple substances, like oxygen, iron or sulphur, are themselves compounds. By their very idea, then, simple substances cannot be decomposed.

Now put this beside the law of conservation of matter. If no simple substance can be made, destroyed, or turned into another, then the amount of each simple substance stays constant through all chemical changes. That gives the balance sheet a new and far more important meaning. It is not only the total weight that must match on both sides; the weight of each simple substance must match on its own. If we know how much of each simple substance is in the substances we start with, then all the new compounds that arise can hold only that same amount of each. So, Mendeleev says, the essence of chemical change comes down to studying what each simple substance is joined with, and how, before the change and after it. It is like a bank that keeps separate accounts in pounds, euros and dollars: money may move between customers all day, but at closing time each currency must add up on its own.

To write such balance sheets compactly, chemists agreed on symbols. Each simple substance is marked by one or two first letters of its Latin name. Oxygen, oxygenium, is marked by a capital O; nitrogen, nitrogenium, by a capital N; mercury, hydrargyrum, by an H and a g; iron, ferrum, by an F and an e. A compound is written by setting side by side the letters of the simple substances it is made of, so the red mercury oxide is written as the letters for mercury followed by the letter O. On top of that, each letter stands for a definite relative weight of its simple substance, called its share or its atomic weight. So a formula tells you not only which simple substances are in a compound

but how much of each. Every chemical process can be written as an equation of such formulas, and the weight of each simple substance must be the same on both sides, because none is made and none is lost.

O OXYGENIUM

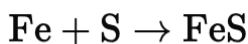
N NITROGENIUM

HgO

Hg HYDRARGYRUM

RED MERCURY OXIDE

Fe FERRUM



Letters from Latin names

Mendeleev then shows how a formula gives the composition in per cent. Picture a compound of two simple substances. The formula says how many shares of the first it contains, and how many shares of the second. Multiply the number of shares of the first by the weight of one share, and you have the weight of the first in the compound; do the same for the second. The per cent of the first is then its weight divided by the total weight of both, times one hundred; and likewise for the

second. In words: each part's share of the whole, counted out of a hundred.

$$\%_1 = \frac{n_1 a_1}{n_1 a_1 + n_2 a_2} \times 100$$

$$\text{Na} = 23$$

$$\text{Cl} = 35.5$$

$$\text{NaCl} = 58.5$$

$$\frac{23}{58.5} = 39.3\%$$

$$\frac{35.5}{58.5} = 60.7\%$$

IN 100 G OF SALT

Na 39 g	Cl 61 g
---------	---------

Per cent from a formula

Now a calculation aloud, with Mendeleev's own example, table salt. Its formula says one share of sodium and one share of chlorine. A share of sodium weighs twenty-three, and a share of chlorine thirty-five and a half. Together that is fifty-eight and a half. Sodium's part is twenty-three out of fifty-eight and a half, which comes to thirty-nine point three per cent. Chlorine's part is thirty-five and a half out of fifty-eight and a half, sixty point seven per cent. The two add up to a hundred, as they must. So if you are given a real weight of the compound, the formula tells you the real weights of the simple substances in it: a hundred grams of salt hold about thirty-nine grams

of sodium and sixty-one of chlorine. A one-kilogram bag of kitchen salt therefore holds close to four hundred grams of sodium, a soft metal that would fizz on water if you could get it out.

This clearly limits what chemical change can do. From bodies of given quality you can get not every possible body, but only those that contain the very same simple substances. Yet even with this first limit, the number of compounds that could form is endlessly large, and only a comparatively small number has been studied and described.

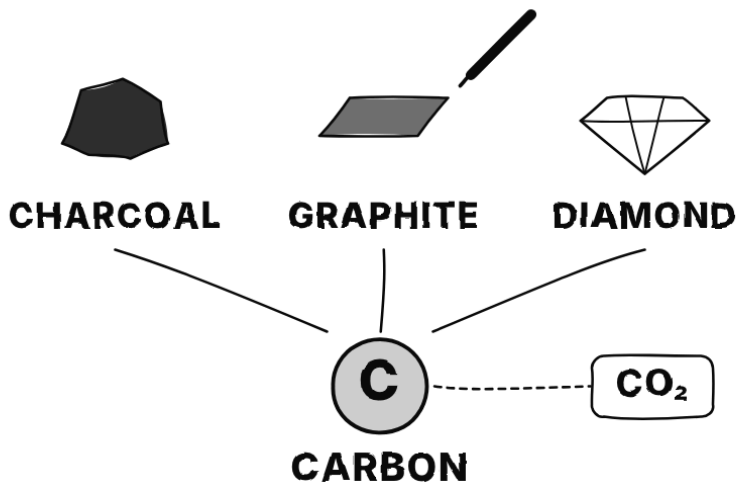
Anyone starting work can easily discover a new compound, and many new ones are foreseen by science before they are made. Science, Mendeleev says, lies in grasping the uniformity hidden in this multitude, and its aim is to understand the laws that govern how compounds form and what properties they have.

Here Mendeleev makes a careful distinction. When we say that red mercury oxide contains oxygen, we do not mean that oxygen, as a gas, sits inside the powder. We mean only what the oxide can do: that mercury and oxygen can be obtained from it, and that it can pass them on to other bodies. In short, the composition of a compound is an expression of the changes it is capable of. So the red oxide contains not two simple substances, a metal and a gas, but two elements, mercury and oxygen, which separately give the metal and the oxygen gas. It contains only the substance of these simple bodies, Mendeleev says, as steam contains the substance of ice but not ice itself, or as bread contains the substance of grain but not the grain. Your table sugar holds the element carbon, but no charcoal is hidden among the crystals.

An element can be recognised even without knowing its simple substance, just from its compounds. For a long time fluorine had not

been obtained on its own, yet it had to be counted an element, because its compounds with other simple substances were known, and they differed from all other similar compounds.

Two more facts make the difference between element and simple substance still clearer. First, compounds can themselves join into still more complex compounds, and then be pulled back out of them by the same methods used to free simple substances; so being extracted does not by itself make something simple. Second, many simple substances exist in several forms, while the element is something that does not change. Carbon appears as charcoal, graphite and diamond, which are different bodies, and each is a simple substance, yet the element is one. That same carbon is present in carbon dioxide, and yet that gas holds neither charcoal, nor graphite, nor diamond. The grey core of a pencil and the stone in a diamond ring are two very different simple substances of a single element.



Three bodies, one carbon

Remember

No simple substance has ever been seen to turn into another, so one metal cannot be made into another. Together with the conservation of matter, this means the amount of each simple substance stays the same through every chemical change.

Formulas write compounds with Latin letters, each standing for a definite share by weight, so they show both what a compound contains and in what per cent: table salt is about thirty-nine per cent sodium and sixty-one per cent chlorine. The composition of a compound expresses what changes it can undergo; red mercury oxide holds the elements mercury and oxygen, not the metal and the gas. A simple substance can take several forms, as carbon does in charcoal, graphite and diamond, while the element beneath them stays one and unchanged.

Questions

1. Why does the amount of each simple substance stay the same through every chemical change?
 - a. Because simple substances are too heavy to take part in reactions.
 - b. Because a simple substance can be neither made, destroyed nor turned into another, and matter is conserved.
 - c. Because chemists always add back what is lost.
 - d. Because compounds always contain equal amounts of each simple substance.

2. What does a chemical formula tell you that a plain list of simple substances does not?
 - a. How much of each simple substance is in the compound, because each symbol stands for a definite weight.
 - b. The colour and smell of the compound.
 - c. How hot the compound must be heated to decompose.
 - d. Which compounds can never be made in a laboratory.
3. From iron and sulphur alone, which of these could a chemist possibly obtain?
 - a. Copper sulphide, since copper is close to iron.
 - b. A compound of sulphur and oxygen, using the sulphur only.
 - c. Only compounds made of iron and sulphur, and nothing containing any other simple substance.
 - d. Gold, if the reaction is carried out cleverly enough.
4. Charcoal, graphite and diamond are different bodies. How does Mendeleev describe their relation?
 - a. They are three different elements with similar names.
 - b. Only diamond is a simple substance; charcoal and graphite are compounds.
 - c. They are compounds of carbon with differing amounts of oxygen.
 - d. They are different simple substances of one and the same unchanging element, carbon.

Answers

1. b) Joining the conservation of matter with the fact that no simple substance can be made, broken down or changed into another, each one

must come out in exactly the amount it went in.

2. a) Each symbol stands for a definite relative weight, its share, so the formula shows both what the compound contains and in what amounts.

3. c) From bodies of given quality one can get only bodies containing the very same simple substances; neither copper, oxygen nor gold is among them.

4. d) Many simple substances exist in several forms while the element stays one: charcoal, graphite and diamond are three bodies, but the element is carbon.

Worked examples

Table salt in per cent Table salt has one share of sodium and one of chlorine; a share of sodium weighs 23 and a share of chlorine 35.5. What per cent of the salt is sodium, and what per cent chlorine?

The weight of sodium in one formula of salt is one share times 23, that is 23; of chlorine, 35.5.

The whole compound then weighs 23 plus 35.5, that is 58.5.

Sodium's per cent is 23 divided by 58.5, times 100, which is 39.3.

Chlorine's per cent is 35.5 divided by 58.5, times 100, which is 60.7; the two add up to 100.

Answer: 39.3 per cent sodium and 60.7 per cent chlorine

Practice

1. Using Mendeleev's figures for table salt, how many grams of sodium are in 200 grams of salt?

Hint: Salt is 39.3 per cent sodium; take that share of 200.

Answer: About 78.6 grams. 39.3 per cent of 200 grams is 0.393 times 200, which is 78.6 grams; the remaining 121.4 grams are chlorine.

2. An imagined compound contains two shares of a simple substance A and one share of a simple substance B. A share of A weighs 10 and a share of B weighs 30. What per cent of the compound is A?

Hint: First find the weight of A in the compound: number of shares times the weight of one share.

Answer: 40 per cent. A contributes 2 times 10, that is 20; B contributes 30; the whole is 50. A's per cent is 20 divided by 50, times 100, which is 40.

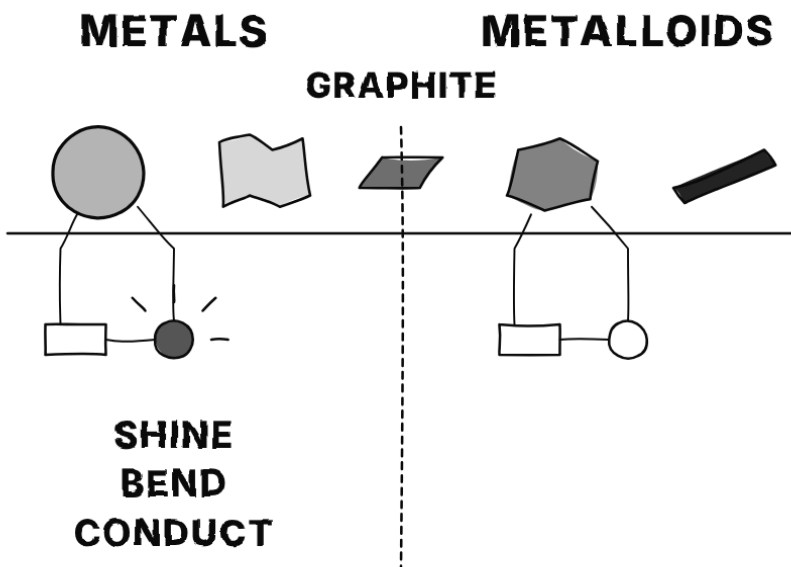
3. Explain why fluorine was counted as an element even before anyone had obtained it on its own.

Hint: Think about what chemists already knew of its compounds.

Answer: An element can be recognised from its compounds alone. Fluorine's compounds with other simple substances were known and differed from all other similar compounds, so they had to contain a distinct, unchanging element.

Seventy-Seven Bricks and the Force That Binds Them

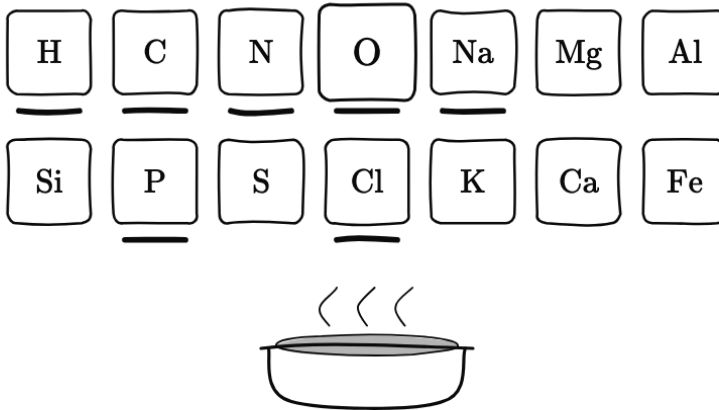
Lay four things on a table: a copper coin, a yellow lump of sulphur, a stick of charcoal and a strip of aluminium foil. Hold each to the light, try to bend it, touch it to your lip, and connect it between a battery and a small bulb. The coin and the foil shine, bend without snapping, feel cold, and light the bulb. The sulphur is dull, crumbles, feels warm, and the bulb stays dark. That simple test is the first sorting Mendelev offers among the simple substances, and he immediately warns us not to trust it too far.



Many simple substances, though not all, have a special lustre, are opaque, can be hammered out, and conduct heat and electricity very well. These are the properties of metals and of their mixtures with one another, which are called alloys. Simple substances without the physical signs of metals are called metalloids, which in Mendeleev's day meant what we now call non-metals. In sharp examples, such as copper beside sulphur, the two kinds are clearly different. But in many particular cases the difference is not sharp, and so it cannot serve as the basis for an exact division of the simple substances into two groups. The grey core of a pencil shows the problem: graphite is no metal, yet it has a soft shine and conducts electricity well enough to be used in modern batteries.

Whatever the sorting, the ideas of element and simple substance are the foundation of chemistry, and Mendeleev gives a list of the simple substances right at the start to show the state of knowledge. About eighty simple substances are recognised. Some of them, about six, are so rare and have been obtained in such small amounts that what is known of them is sometimes thin and incomplete. The common bodies of nature contain only a very small number of simple substances, and these are the best studied, simply because more researchers could experiment with them.

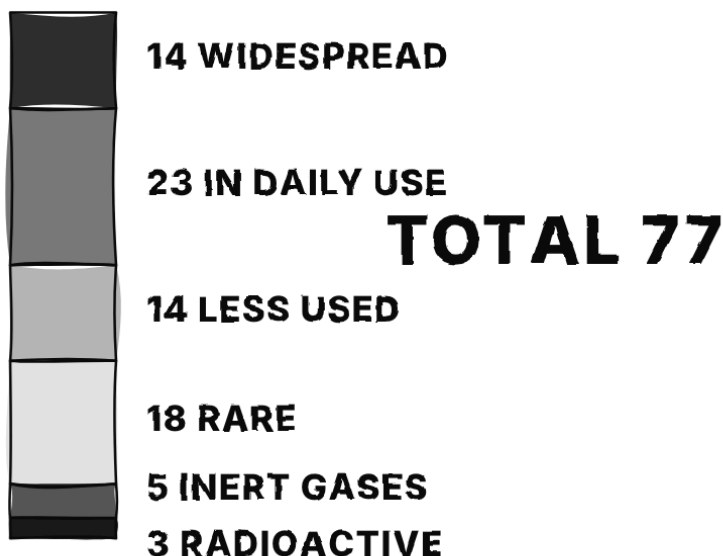
≈ 80 KNOWN



The fourteen commonest

The most widespread are fourteen. Hydrogen is in water and in living things. Carbon is in living things, in coal and in limestone. Nitrogen is in the air and in living things. Oxygen is in air, water and the earth, and of all of them its mass is the greatest. Sodium is in table salt and many stones; magnesium in sea water and stones; aluminium in stones and clay; silicon in sand, clay and stones. Phosphorus is in bones, plant ash and soil; sulphur in pyrites, gypsum and sea water; chlorine in table salt and sea water. Potassium is in stones, plant ash and saltpetre; calcium in limestone, gypsum and living things; and iron in soil, iron ores and living things. A bowl of salted soup on your kitchen table already holds most of these: hydrogen and oxygen in the water, sodium and chlorine in the salt, carbon, nitrogen, phosphorus and the rest in the food.

A second list holds simple substances that are not very widespread in nature but whose compounds are used in daily life or industry. Lithium is used in medicine and photography; boron in borax and boric acid; fluorine in fluorspar and in the acid that etches glass. Chromium and manganese give strongly coloured compounds used as oxidisers; cobalt colours glass blue; nickel is plated onto other metals. Copper, the familiar red metal; zinc, in sheets, in galvanic cells and in brass; and arsenic, whose white oxide is a poison. Bromine is a brown, volatile liquid; strontium gives the red of Bengal fires; silver is the familiar white metal; cadmium gives a yellow paint. Tin, antimony in alloys such as printer's type, iodine in medicine and photography, barium in heavy spar and as an additive to white paint. And finally platinum, gold, mercury and lead, metals everyone knows, and bismuth, used in medicine and in alloys that melt at low temperature. The battery in your phone carries lithium, and the galvanised bucket in your shed is iron with a coat of zinc: two items from Mendeleev's second list in a modern home.



Counting to seventy-seven

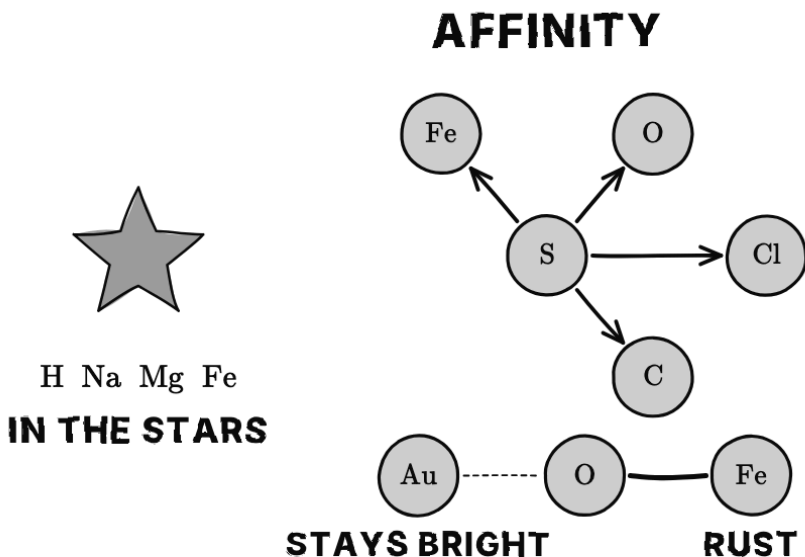
A third list is less used, though well known and fairly often met in nature in small amounts: beryllium, titanium, vanadium, selenium, zirconium, molybdenum, palladium, cerium, tungsten, osmium, iridium, thallium, thorium and uranium. A fourth list is rarer still and has no practical use, though its compounds have been studied fairly fully: among them scandium, gallium, germanium, rubidium, caesium and lanthanum, and a group of very similar rare earths.

Then comes a group unlike all the others: the gases found by Ramsay, present in small amounts in the air. They are helium, neon, argon, krypton and xenon, and what sets them apart is that no compound of any of them with another element had yet been made. There is also some ground for counting as separate the metals actinium, polonium

and radium, the last discovered by Madame Curie, found in the so-called radioactive compounds that occur as small admixtures in ores of uranium and thorium. The red glow of a neon sign is one of Ramsay's gases at work, chosen precisely because it hardly reacts with anything.

Here is a count aloud. Fourteen widespread substances, plus twenty-three in everyday use, makes thirty-seven. Add fourteen less used ones and you have fifty-one; add eighteen rare but studied ones and you reach sixty-nine. Five of Ramsay's gases bring it to seventy-four, and the three radioactive metals to seventy-seven. That is exactly the number Mendeleev gives, and beyond these seventy-seven he names a few more, gadolinium, terbium, thulium, holmium and others, whose properties are still little known, and whose independence is not fully established.

Are these the substances of the Earth alone? No: the presence of many of the commonest of them, such as hydrogen, sodium, magnesium and iron, has been proved beyond doubt on distant heavenly bodies, by studying their light. This convinces us that the form of matter appearing on Earth as simple substances spreads far through the universe. Why some simple substances are so much more plentiful in nature than others, Mendeleev says, we do not yet know.



Same bricks, different appetites

The basic character of each element is its ability to combine with others into compounds, more or less stable, and inclined to form still more complex ones. Sulphur, for instance, combines easily with metals, with oxygen, with chlorine and with carbon. Silver and gold combine with difficulty, and many of their compounds are unstable and easily decompose on heating. The cause or force that pushes substances to chemical change must at the same time be the cause that holds different elements together in a compound and gives it a certain stability. That cause is called affinity, or chemical affinity. A gold ring lost in a field for a century comes up shining, while an iron nail beside it crumbles to rust: affinity, seen in the soil.

What is this force? It must be thought of as purely attractive, like gravity, and so some scientists, Bergman at the end of the eighteenth century and Berthollet at the start of the nineteenth, supposed that affinity might in essence be the same as universal gravitation, acting only at the smallest distances. But affinity cannot be wholly identified with gravitation, because gravitation depends only on mass and distance, not on the kind of substance, while affinity depends on it strongly. Nor can it be identified with cohesion, the force that gives a uniform solid its crystal form, elasticity and hardness, and gives a liquid its surface, its drops and its rise in narrow tubes. Cohesion acts between particles of the same substance, affinity between different substances, though both act only at imperceptibly small distances and have much in common.

Nor is affinity the same as the forces that make different bodies cling: two flat polished plates sticking together, a liquid wetting a solid, a gas thickening on a solid surface. In a chemical change one body penetrates the other and a new one forms, which does not happen in mere sticking. Still, these clinging forces, which act only on full contact, are a transition from mechanical forces to chemical ones. A drop of water clinging to a window is sticking, not reacting: the glass and the water both stay what they were.

For a long time, especially in the first half of the nineteenth century, chemical attraction was identified with electrical forces. The two are closely linked: chemical interactions produce electricity, and electricity strongly affects chemical processes, as when a galvanic current decomposes compounds. But chemistry is linked just as closely with heat: heat is given off in chemical changes, and heat can decompose bodies. Such links only show the unity of the forces of nature, the ability of one force to produce another, to turn into it and

to change it. So the identification of chemical forces with electrical ones did not survive experimental testing.

Of all the molecular phenomena of nature, heat is the most completely understood, reduced to the basic mechanical ideas of energy, equilibrium and motion that have been open to strict mathematics since Newton. So it is natural, Mendeleev says, especially in recent decades, to try to bring chemical ideas into strict relation with the phenomena of heat, though without treating chemical phenomena as heat phenomena. The nature of chemical forces is as hidden from us as the nature of gravitation. But just as astronomy, without knowing what gravitation is, learned to describe and predict the heavens in great detail with mechanical ideas, so chemistry may hope for real progress through the mechanical theory of heat.

That part of chemistry is still being worked out and is developed in a separate branch, called theoretical or physical chemistry, and best called chemical mechanics. It takes for granted that you already know the many substances, the changes they undergo, and the phenomena that go with them. So, Mendeleev concludes, one can come to chemical mechanics only after learning the basic ideas and substances of chemistry, and that is the main aim of his book.

Remember

Metals shine, are opaque and malleable, and conduct heat and electricity; metalloids lack these signs; but the line is blurred and cannot divide the simple substances exactly. About eighty simple substances were recognised: fourteen widespread, with oxygen the most massive, then those used in daily life, rarer ones, Ramsay's gases with no known compounds, and the radioactive metals, seventy-seven in all, plus a few uncertain ones. The same simple substances are found in the light of distant stars. Each element is marked by its readiness to combine; the force behind it, chemical affinity, is not gravitation, cohesion, sticking or electricity, though linked with heat and electricity. Its nature is hidden, and chemical mechanics, which studies it through the theory of heat, must come after knowing the substances themselves.

Questions

1. Why can the metal and metalloid split not serve as an exact division of the simple substances?
 - a. Because metalloids turn into metals when heated.
 - b. Because in many particular cases the physical signs of a metal are present only in part, so the line is blurred.
 - c. Because there are more metalloids than metals.
 - d. Because metals and metalloids cannot form compounds with each other.

2. What sets Ramsay's gases, such as helium and argon, apart from all the other simple substances?
 - a. No compound of any of them with another element had yet been made.
 - b. They are the most widespread substances in nature.
 - c. They are radioactive.
 - d. They are metals that happen to be gases.
3. Why can chemical affinity not be the same thing as cohesion, though both act only at tiny distances?
 - a. Because cohesion acts only in liquids.
 - b. Because affinity depends only on mass and distance.
 - c. Because cohesion pushes particles apart.
 - d. Because cohesion acts between particles of the same substance, affinity between different substances.
4. Chemical change produces electricity, and a current can decompose compounds. Why did Mendeleev still reject the idea that chemical forces are electrical?
 - a. Because electricity was not yet understood at all.
 - b. Because chemistry is linked just as closely with heat, and such links only show that the forces of nature can produce one another.
 - c. Because a current can never decompose any compound.
 - d. Because chemical changes never produce electricity in practice.

Answers

1. b) In sharp examples like copper and sulphur the difference is clear, but in many cases it is not sharp, so it cannot be a basis for exact division.

2. a) They occur in small amounts in the air, and unlike every other simple substance, none of their compounds had been obtained.

3. d) Cohesion gives a uniform solid its form and a liquid its drops, acting within one substance; affinity acts between different substances and makes something new.

4. b) Heat is tied to chemical change just as closely as electricity; these ties show the unity of the forces of nature, and the electrical identification failed under testing.

Practice

1. Mendeleev's lists name 14 widespread simple substances, 23 used in daily life, 14 less used, 18 rare but studied, 5 gases found by Ramsay and 3 radioactive metals. Check that this gives his total.

Hint: Add the groups one at a time.

Answer: 77. Fourteen plus twenty-three is 37; plus fourteen is 51; plus eighteen is 69; plus five is 74; plus three is 77, the number Mendeleev gives before naming a few uncertain ones beyond it.

2. Explain how a polished pair of plates sticking together differs from a chemical change, and why Mendeleev still sees such sticking as a link between mechanical and chemical forces.

Hint: Ask whether a new substance forms, and at what distance the forces act.

Answer: When plates stick, each stays what it was; in a chemical change one body penetrates the other and a new substance forms. But the clinging forces, like chemical ones, act only at full contact, so they form a transition between mechanical and chemical forces.

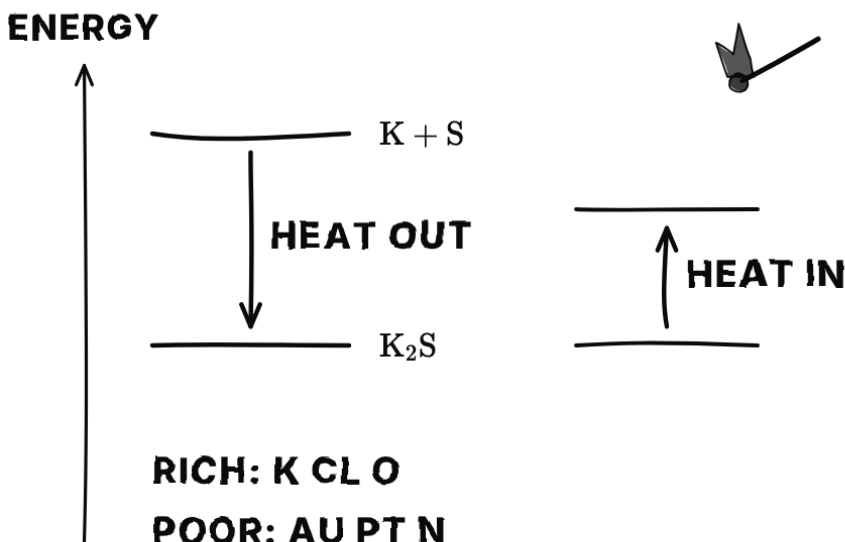
3. Why does Mendeleev hope chemistry can progress through the theory of heat even though the nature of chemical force is unknown?

Hint: Think of how astronomy managed without knowing what gravitation is.

Answer: Heat is the best understood molecular phenomenon, reduced to mechanical ideas of energy, equilibrium and motion. Just as astronomy predicted the heavens with mechanical ideas without knowing what gravitation is, chemistry may advance through the mechanical theory of heat without knowing what affinity is.

The Hidden Store of Chemical Energy

Strike a match. A moment ago it was a cold stick with a pink head; now it gives off heat and light that were nowhere to be seen. The heat did not come from nothing, because energy is never created. So it must have been waiting, hidden, in the substances of the match head and the air. That is where Mendeleev now takes us: to the energy that substances carry inside them.



The hidden store of energy

His argument has three steps. Chemical changes come from inner forces belonging to the substances themselves. Chemical phenomena

always consist in the motion of material particles. And the study of mechanics and physics has established that energy is conserved: it changes form, but is never lost or made. So we must admit that substances, and elements in particular, hold a store of chemical energy, an invisible motion that urges them to react. If a reaction gives off heat, part of the chemical energy has passed into heat; if a reaction takes in heat, part of that heat has gone into hiding as chemical energy. A rechargeable battery makes this visible: plugging it in pushes energy into its chemicals, and running your phone lets them spend it again, warming the phone a little as they do.

This store can run down. After several combinations, each of which gives off heat, the compound may have so little energy left that it is sluggish, an unenergetic body. Yet such a body can sometimes combine with an energetic simple or compound substance, and give still more complex bodies that are once more able to react. Among the simple substances, gold, platinum and nitrogen have little energy; potassium, chlorine and oxygen have a great deal.

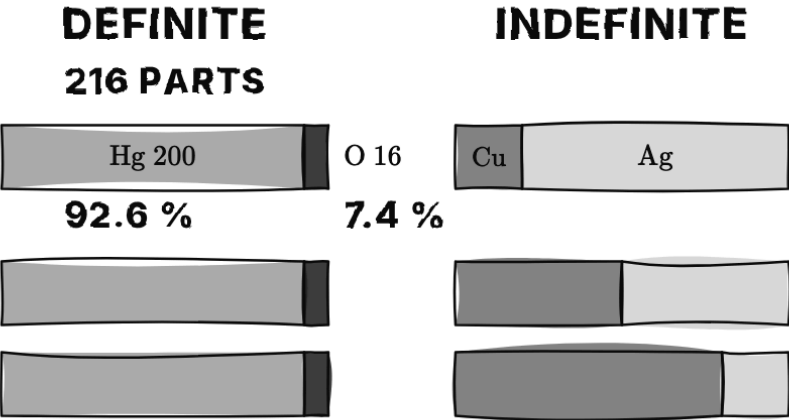
Unlike substances that combine often give a product with reduced energy. Potassium and sulphur both burn easily in air once they are heated. But once they have combined with each other, the compound, though it can still be oxidised, does not burn in air as its separate parts do. Part of the energy of potassium and sulphur was given off as heat when they joined. Just as some heat is taken in or given out when a substance passes from one state to another, as from ice to water, so in every combination, decomposition and other chemical process the store of chemical energy changes, and heat is given out or taken in with it.

To understand chemical change mechanically, that is, to study how reactions run, Mendeleev lists five kinds of knowledge as especially important. The first is stoichiometry, the part of chemistry that studies the quantitative relations, by weight and by volume, between reacting substances. The second is telling apart the different kinds and classes of chemical interaction. The third is studying how properties change as composition changes. The fourth is the phenomena that accompany chemical change, and the fifth is a general view of the conditions in which reactions happen.

Stoichiometry is worked out very fully. Its laws, found by Dalton, by Avogadro and Gerhardt, and by others, reach so deep into all of chemistry that its present state can be called the age of their detailed application to particular cases. Expressing the composition of bodies by weight and by volume is still the main task of chemical research, so the rest of Mendeleev's book is ruled by these laws. Even the meaning of combination, decomposition and displacement gained a new character from exact ideas about the amounts that react. And from these ideas came a new division of compounds into definite and indefinite ones.

Early in the nineteenth century Berthollet made no such distinction. But Proust showed that very many compounds contain their parts in a quite exact proportion by weight, which does not change under any conditions. Red mercury oxide, for example, contains sixteen parts by weight of oxygen for every two hundred parts of mercury. Here is a calculation aloud. Two hundred plus sixteen is two hundred and sixteen parts of oxide. Oxygen's share is sixteen out of two hundred and sixteen, about seven point four per cent; mercury's share is two hundred out of two hundred and sixteen, about ninety-two point six

per cent. So any sample of red mercury oxide, from any laboratory, is about ninety-three per cent mercury.



$200 + 16 = 216$

In an alloy of copper and silver, on the other hand, one can add any amount of either metal, just as one can change the proportion of sugar and water in a solution, and still get a uniform whole with the combined properties of its parts. These are indefinite compounds. In nature and in laboratory and factory practice, alloys and solutions play as important a role as definite compounds, but since the laws of proportion had been applied mostly to definite ones, knowledge of indefinite compounds was less complete, and only in recent years had researchers turned to them. The sweetness of your tea is up to you, an indefinite compound; but the water in the cup has the same fixed

proportion of hydrogen and oxygen whether it comes from a tap in Moscow or a spring in the Alps.

For chemical mechanics it is very important to tell reversible from irreversible reactions. Substances that can react at a given temperature give bodies which, at the same temperature, may or may not give back the starting substances. Salt dissolves in water at ordinary temperature, and at that same temperature the solution can give back the salt as the water evaporates. Carbon disulphide forms from sulphur and charcoal at a temperature at which it can also split back into sulphur and charcoal. Iron at a certain temperature frees hydrogen from water and forms iron oxide, and at that same temperature the oxide with hydrogen can give iron and water.



EQUILIBRIUM

gunpowder



gases + smoke

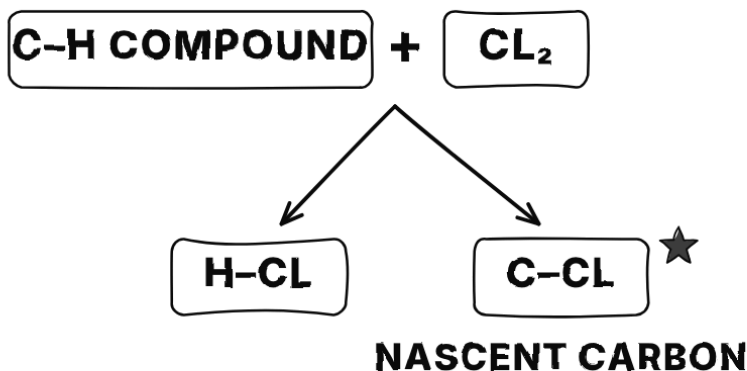
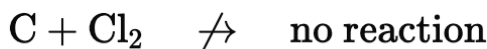


Both ways, or one way

Here is what follows, told in words. Suppose two substances give two others, and those two others can give back the first two. Then whether you start from a given mass of the first pair or from the corresponding mass of the second pair, you end with all four substances together, in chemical equilibrium. Increase the amount of one of them, and the balance settles in a new place, so reversible reactions let us study how the mass of a substance influences the course of a change.

Many reactions of very complex compounds and mixtures are irreversible. Many complex substances of plants and animals fall apart in heat, and their products never give back the original substance, at any temperature. Gunpowder, a mixture of saltpetre, sulphur and charcoal, burns into gases and smoke that at no temperature give back the starting substances. Toast is a kitchen example: no temperature will turn the browned crust back into fresh bread.

To obtain such substances one needs a roundabout way. If one substance will not combine directly with another under any conditions, that does not mean their compound cannot exist. Often the first can be joined to a third substance, and the second to a fourth; and if the third has a strong affinity for the fourth, then when the two compounds act on each other, the third and fourth pair off, and the first and second are left to join as well. The first and second are then in a special, freshly released state, and it is thought that they combine precisely because they meet at the moment of release, in the nascent state.



Carbon meets chlorine sideways

Chlorine is Mendeleev's example. It does not react directly with charcoal, graphite or diamond, the forms of free carbon, yet compounds of chlorine and carbon exist and many are very stable. They are made by letting chlorine act on compounds of carbon and hydrogen. The chlorine takes away the hydrogen, and the carbon, freed at that moment, joins with part of the chlorine, so in the end the chlorine is combined with both hydrogen and carbon.

Remember

Substances hold a store of chemical energy, an invisible motion urging them to react; heat given off by a reaction comes from that store, and heat taken in is hidden in it. Gold, platinum and nitrogen have little energy, potassium, chlorine and oxygen much; unlike substances often combine into a product less energetic than its parts. Stoichiometry, the study of the proportions in which substances react, is the best developed part of chemistry, and divides compounds into definite ones, like red mercury oxide with sixteen parts of oxygen to two hundred of mercury, and indefinite ones like alloys and solutions. Reversible reactions run both ways and reach a chemical equilibrium that shifts with the amounts present; irreversible ones, like burning gunpowder, run one way only. Substances that will not combine directly can sometimes be joined by a roundabout route, meeting in the nascent state, as chlorine and carbon do.

Questions

1. A reaction takes in heat from its surroundings. Where, in Mendeleev's view, has that heat gone?
 - a. It has been destroyed by the reaction.
 - b. It has escaped as light.
 - c. It has passed, at least in part, into the chemical energy of the products.
 - d. It has been turned into extra weight of the products.

2. What did Proust show that Berthollet had not distinguished?
 - a. That many compounds hold their parts in a fixed proportion by weight, unlike alloys and solutions.
 - b. That every compound can be split by heat.
 - c. That alloys are simple substances.
 - d. That gases have no weight.
3. In a reversible reaction, what happens if you increase the amount of one of the substances?
 - a. The reaction becomes irreversible.
 - b. Nothing changes, because the balance is fixed.
 - c. All the other substances disappear.
 - d. The balance settles in a new place, which lets us study how mass affects the change.
4. Chlorine and carbon do not combine directly, yet their compounds exist. Why does the roundabout route work?
 - a. Because chlorine turns into carbon when it meets hydrogen.
 - b. Because carbon set free from its compound with hydrogen is in the nascent state and especially ready to combine.
 - c. Because diamond dissolves in chlorine at high temperature.
 - d. Because hydrogen gives its energy to the chlorine.

Answers

1. **c)** Energy is conserved; heat taken in by a reaction hides, in part, as chemical energy stored in the substances formed.
2. **a)** Proust found that many compounds contain their parts in an exact proportion that never changes, which separates definite compounds from

indefinite ones.

3. d) Adding more of one substance gives new conditions of equilibrium, so reversible reactions show the influence of mass on chemical change.

4. b) Chlorine takes away the hydrogen, and the carbon freed at that moment, in the nascent state, joins with part of the chlorine.

Worked examples

The fixed proportion of red mercury oxide Red mercury oxide contains 16 parts by weight of oxygen for every 200 parts of mercury. What per cent of the oxide is oxygen, and what per cent mercury?

The proportion is fixed, so take any sample as 200 parts of mercury and 16 of oxygen.

Together that is 216 parts of oxide.

Oxygen's share is 16 out of 216; times 100 that is about 7.4 per cent.

Mercury's share is 200 out of 216, about 92.6 per cent; the two make 100.

Answer: About 7.4 per cent oxygen and 92.6 per cent mercury

Practice

1. Using the fixed proportion of 16 parts of oxygen to 200 of mercury, how much oxygen can be obtained by completely decomposing 54 grams of red mercury oxide?

Hint: Oxygen is 16 parts in every 216 parts of oxide.

Answer: 4 grams. 54 grams is a quarter of 216, so the oxygen is a quarter of 16, that is 4 grams, and the mercury is 50 grams.

2. A jeweller makes two copper and silver alloys, one with much more silver than the other, and both are uniform. A chemist makes red

mercury oxide twice and always finds the same proportion of mercury to oxygen. Explain the difference.

Hint: Think of definite and indefinite compounds.

Answer: The alloy is an indefinite compound: either metal can be added in any amount and the whole stays uniform. Red mercury oxide is a definite compound: its parts are always in the same fixed proportion by weight, whatever the conditions.

3. Potassium and sulphur each burn in air once heated, but their compound does not. Explain this using the idea of a store of chemical energy.

Hint: What was given off when the two combined?

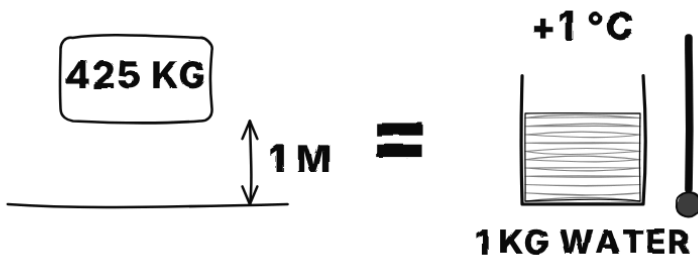
Answer: When potassium and sulphur combined, part of their store of chemical energy was given off as heat. The compound is left with less energy, so although it can still be oxidised, it no longer burns in air as its parts do.

Heat Opens and Closes the Door

A lump of charcoal can lie in the open air for years without burning, though the oxygen it needs is touching it all the time. Hold a flame to one corner until it glows, and the fire creeps on by itself until only ash remains. The substances were there all along; something else had to change. Before Mendeleev turns to what that something is, he looks at the traffic that runs both ways between chemistry and physics.



motion $\leftrightarrow$ current



$$1 \text{ L, } +80^{\circ}\text{C} = 34 \text{ t} \times 1 \text{ m}$$

425 kilogram-metres = 1 unit of heat

In chemical processes, he says, there is not only movement of particles, but heat, light, electrical tension and galvanic current. And

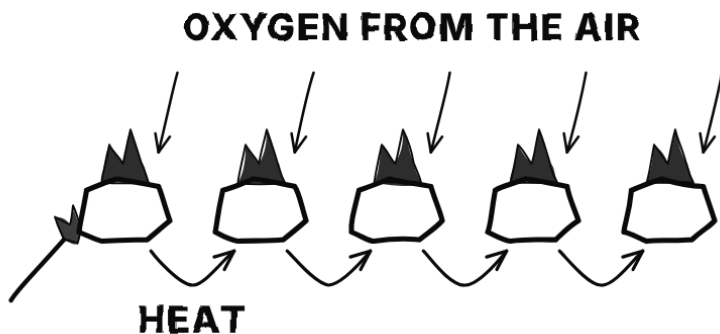
each of these, in its turn, can alter chemical changes. This two-way action, or reversibility, comes from the fact that all the phenomena of nature are only different kinds and forms of motion, visible or invisible, molecular motion. Physics had shown that sound, and then light, are in essence vibrations.

The tie between heat and mechanical work also ceased to be a guess and became certain, and it was measured. Mendeleev gives the number: four hundred and twenty-five kilogram-metres of mechanical work correspond to one kilogram unit of heat, a calorie in his sense. Here is what that means, said aloud. A kilogram-metre is the work of lifting one kilogram by one metre. So lifting four hundred and twenty-five kilograms by one metre is as much work as the heat that warms one kilogram of water by one degree. Or, the other way round, a one-kilogram weight would have to fall four hundred and twenty-five metres to warm one kilogram of water by a single degree, if all its work turned into heat. That is why a kettle on an electric hob needs so much energy: warming a litre of water by eighty degrees takes as much work as lifting thirty-four tonnes by a metre.

Electricity, too, can be had from mechanical work, both static electricity and current, as in Gramme's dynamo; and current, in an electric motor, gives mechanical motion back. Send a current through Gramme's machine and it spins; spin it, and it gives a current. So chemical mechanics must take the main lines of its development from these ties between chemical, physical and mechanical phenomena. But Mendeleev is frank: the subject, complex and new, has no orderly theory yet, not even a satisfactory hypothesis, so he leaves it as a separate branch, physical chemistry, and does not dwell on it. An electric car does the same two-way trick: its motor drives the wheels

from the battery, and when braking, the turning wheels drive it as a generator.

Now to the charcoal. A chemical change runs in a given direction not only because of the masses, the composition of the bodies and their store of chemical energy, but also because of the conditions the substances are in. For a reaction to happen between substances able to react, many conditions are often needed, sometimes quite unlike those in which substances usually lie in nature. For charcoal to burn, air, and its oxygen, are needed, but the charcoal must also be glowing, heated strongly. The glowing part combines with the oxygen of the air, and the heat given off makes the next parts glow, which burn only because they were heated first. Every reaction, likewise, goes only under certain physical, mechanical and other conditions. A barbecue shows it each summer: the coals sit cold in the bag until a firelighter starts the chain, and then the heat of each coal lights its neighbours.



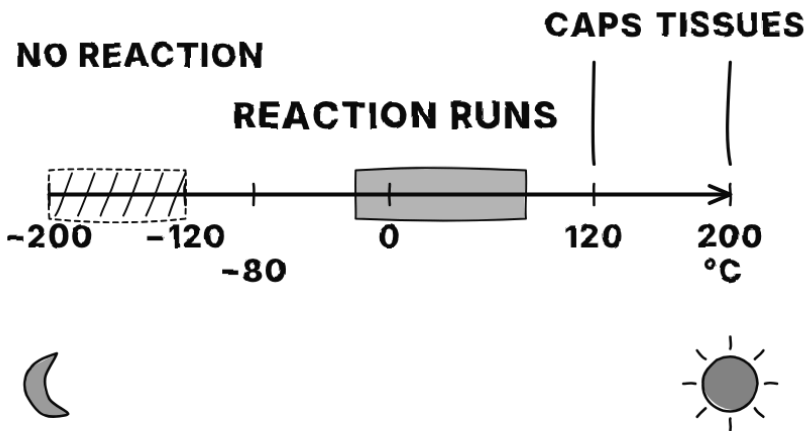
CONDITIONS

Heat passes the fire along

The first condition is the degree of heating. Combinations go on only within certain limits of temperature and not outside them. Burning starts and continues only when the fuel is hot; and, more surprisingly, the compounds of chlorine, or of table salt, with water form only below zero degrees. At higher temperatures these compounds do not form, and once formed they fall apart, wholly or in part.

Why does heating start reactions? One reason is that heat may turn one of the reacting bodies from solid to liquid or vapour, and a liquid helps the reacting particles come into full contact. The other is that heating weakens cohesion, the inner bond between like particles, so the starting bodies come apart more easily and turn into new compounds. When a reaction needs to take in heat, as a

decomposition does, the need for heating is obvious. From all that is known about high temperature, one can now say that every compound decomposes at a strong enough heat.

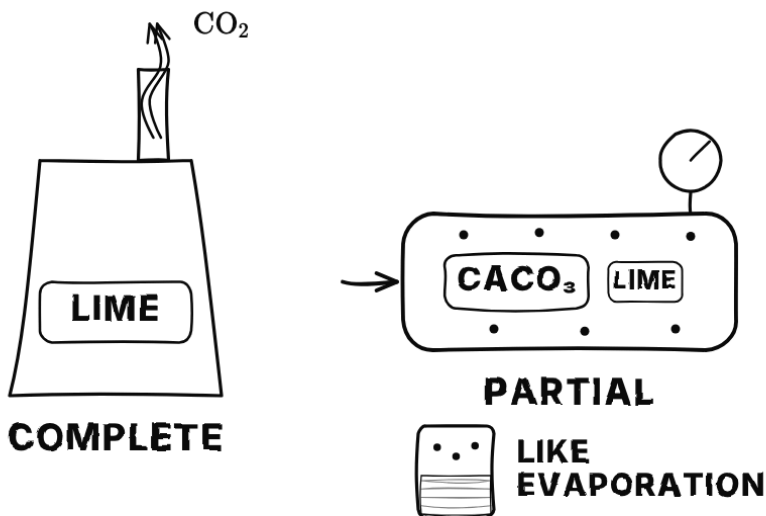


Every reaction has its window

We have already seen red mercury oxide split into mercury and oxygen, and wood fall apart in heat. Some bodies decompose at a mild heat: the fulminating mercury salt put into percussion caps decomposes when heated a little above one hundred and twenty degrees. Many of the substances that make up the tissues of animals and plants decompose at about two hundred degrees. A kitchen oven at two hundred degrees browns a roast for exactly this reason: the substances of the meat begin to break down.

At very low temperatures, on the other hand, no chemical reactions happen at all. We see this in plants, whose chemical processes stop in the winter cold. In eighteen ninety-two Raoul Pictet, using the very low temperatures, down to minus two hundred degrees, reached by boiling liquefied gases, confirmed it. Below minus one hundred and twenty degrees, not even sulphuric acid with caustic soda or with sodium metal reacts, and litmus begins to change colour with acids only above minus eighty. So every reaction needs its own range of temperature, and on the sun, where it is very hot, or on the moon, where it is very cold, many of the changes we see on Earth surely cannot happen.

The effect of heat on reversible reactions is especially instructive. Heat a compound that can re-form from its own products; when decomposition begins, it does not finish at once, neither in time nor in quantity, for a given mass in a given volume. Only a part decomposes; raise the temperature and the decomposed part grows; each temperature, at a given volume, has its own ratio of decomposed to untouched substance, until a temperature is reached where the whole compound falls apart. This incomplete decomposition by heat is called dissociation, and one can distinguish the temperatures at which it begins and ends.



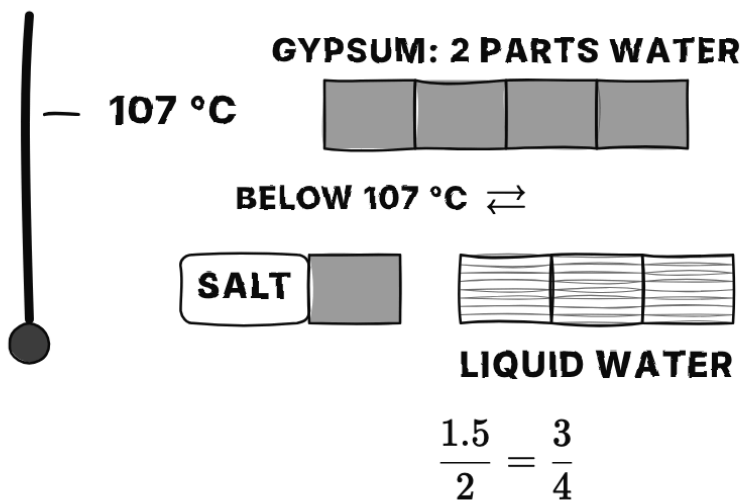
Open kiln, sealed barrel

If one or all of the products do not stay in contact with the undecomposed compound, the decomposition goes to the end. In a lime kiln, limestone breaks down completely into lime and carbon dioxide, because the gas can escape. Seal the same stone in a gun barrel, rivet it shut and heat it, and the gas cannot escape; then at each temperature above the start of dissociation only a share of the stone breaks down. It stops when the carbon dioxide reaches the greatest dissociation pressure belonging to that temperature. Raise the pressure by adding gas, and combination begins again; lower it, and decomposition goes on.

This, Mendeleev says, is just like evaporation. If vapour is not removed, its pressure reaches the greatest value for that temperature,

and evaporation stops. Add vapour, and it condenses to liquid; remove some, keeping the temperature, and evaporation resumes. These ideas of dissociation were introduced by Henri Sainte-Claire Deville. Mendeleev adds that the separated parts combine more easily the nearer their temperature is to the start of dissociation; that temperature is close to the temperature at which they begin to react.

In some cases a chemical change has a quite definite temperature, comparable to a melting or boiling point: above it a compound falls apart, below it the compound forms. It can be seen with a thermometer, and also by the sudden change in volume at that temperature. Natural gypsum is the example: a salt of calcium and sulphuric acid with two parts of water bound in it. At one hundred and seven degrees, in a closed space so that the water cannot fly off as steam, it falls apart completely into a liquid paste: a salt with only half a part of water, and three quarters of the former water as liquid. Here is the arithmetic aloud: two parts of water become half a part, so one and a half parts are set free, and one and a half out of two is three quarters. Below that temperature, the gypsum with two parts of water forms again. Plaster of Paris for a broken arm is gypsum heated to drive off this water; mixed with water again, it sets hard.



Gypsum at 107 °C

Remember

Chemical, thermal, electrical and mechanical phenomena turn into one another because all are forms of motion; four hundred and twenty-five kilogram-metres of work equal one kilogram unit of heat. A reaction depends not only on the substances but on conditions; charcoal burns only once it is heated, and then its own heat keeps it going. Each reaction has its range of temperature: heat helps by bringing particles into contact and weakening cohesion, strong heat decomposes every compound, and deep cold, as Pictet showed, stops reactions altogether. Reversible compounds dissociate partly, a fixed share at each temperature, as limestone does in a sealed barrel, like a liquid evaporating into a closed space. Some changes have a sharp temperature, like gypsum at one hundred and seven degrees, which releases three quarters of its water.

Questions

1. Why does the rest of a lump of charcoal keep burning once one corner has been lit?
 - a. The flame adds oxygen to the charcoal.
 - b. Heat given off by the burning part makes the next parts glow, and they burn only because they are heated.
 - c. Lighting it turns the charcoal into a gas that burns by itself.
 - d. The charcoal's cohesion is destroyed at once by the flame.

2. Limestone breaks down completely in a kiln but only partly in a sealed, heated gun barrel. What makes the difference?
 - a. In the kiln the carbon dioxide escapes; in the barrel it builds up to the dissociation pressure and decomposition stops.
 - b. The barrel is cooler than the kiln.
 - c. Iron from the barrel protects the stone.
 - d. Air in the kiln adds oxygen to the stone.
3. In a sealed barrel of partly dissociated limestone at fixed temperature, what happens if more carbon dioxide is pumped in?
 - a. More limestone decomposes.
 - b. Nothing at all changes.
 - c. Lime and carbon dioxide begin to combine again.
 - d. The lime melts into a paste.
4. What did Pictet's experiments at very low temperatures show?
 - a. That cold makes all reactions faster.
 - b. That acids react with caustic soda at any temperature.
 - c. That litmus changes colour most strongly in extreme cold.
 - d. That below a certain cold even violent reactions do not take place.

Answers

1. **b)** The glowing part combines with oxygen and gives off heat, which heats the next parts; each part burns only because it was heated first.
2. **a)** Decomposition runs to the end only when a product can leave; trapped gas reaches the greatest pressure for that temperature and the breakdown

halts.

3. c) Raising the pressure above the dissociation pressure drives combination, just as adding vapour over a liquid makes it condense.

4. d) Below minus one hundred and twenty degrees not even sulphuric acid with caustic soda or sodium reacts: every reaction needs its range of temperature.

Worked examples

Work and heat 425 kilogram-metres of work correspond to one kilogram unit of heat, the heat that warms one kilogram of water by one degree. How much work corresponds to warming 3 kilograms of water by 2 degrees?

Warming 3 kilograms by 2 degrees needs 3 times 2, that is 6 kilogram units of heat.

Each unit of heat corresponds to 425 kilogram-metres of work.

So the work is 6 times 425.

That is 2550 kilogram-metres, as much as lifting 2550 kilograms by one metre.

Answer: 2550 kilogram-metres

Why gypsum releases three quarters of its water Gypsum holds two parts of water; at 107 degrees in a closed space it becomes a salt with half a part of water, plus liquid water. What fraction of its water is set free?

Before, the salt holds two parts of water; after, half a part.

So the water set free is two minus a half, one and a half parts.

As a fraction of the water it had, that is one and a half out of two.

One and a half out of two is three quarters, as Mendeleev says.

Answer: Three quarters of its water

Practice

1. A 10-kilogram weight falls 85 metres, and all of its work turns into heat. How many kilogram units of heat is that?

Hint: Work in kilogram-metres is weight in kilograms times height in metres; then divide by 425.

Answer: 2 units. The work is 10 times 85, that is 850 kilogram-metres, and 850 divided by 425 is 2 kilogram units of heat.

2. Give Mendeleev's two reasons why heating helps substances to react.

Hint: Think of what heat does to the state of a solid and to the bond between its particles.

Answer: Heat can turn a solid into a liquid or vapour, which helps the particles come into full contact; and it weakens cohesion, the bond between like particles, so the bodies come apart more easily and can form new compounds.

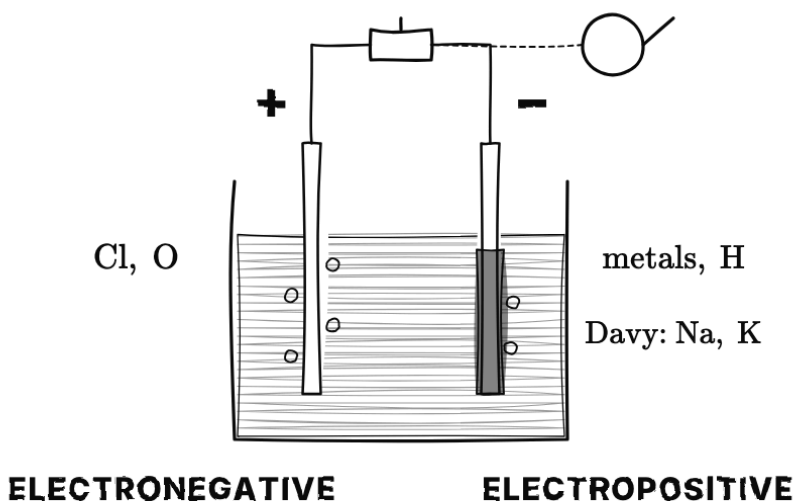
3. Explain why dissociation of limestone in a closed vessel is compared to evaporation of water in a closed space.

Hint: What stops each process, and what restarts it?

Answer: In both, the process stops when the gas or vapour reaches the greatest pressure belonging to that temperature. Adding gas or vapour reverses it, giving combination or condensation; removing some at the same temperature lets decomposition or evaporation continue.

Current, Light, a Blow and a Touch of Platinum

Put two wires from a battery into a glass of salty water. Tiny bubbles start to rise from both wires, and if you look closely, they do not rise in the same way at both ends. Something in the water is being split, and its parts are going to different wires. This is the second condition that steers chemical change, and Mendeleev begins the last stretch of his introduction with it.



Current sorts the parts

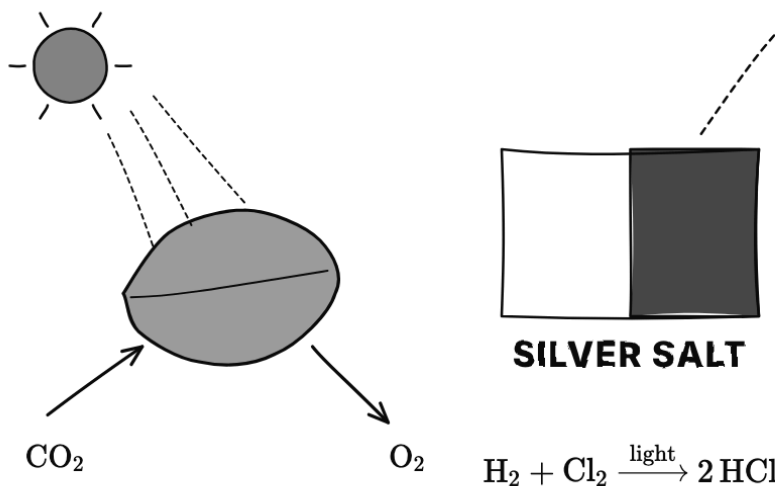
The influence of the galvanic current, and of electricity in general, is very much like that of heat. Most compounds that conduct a current are decomposed by it. And near the conditions where decomposition happens, combinations usually happen too, so electricity can also bring about combination, just as heating can. Electricity, Mendeleev says, should be counted as another kind of particle motion, like heat, so everything said about heat applies to current as well. Its advantage is that splitting a body into its parts can sometimes be done more conveniently, because it happens at ordinary temperature, and even the most stable bodies can be decomposed this way.

There is one important peculiarity. The parts appear at different poles, or electrodes, through which the current passes into the body. Substances that appear at the positive pole, the anode, are called electronegative: mostly non-metals, such as chlorine and oxygen, and also acids and similar bodies. At the negative pole, the cathode, appear metals, hydrogen and similar products of decomposition, called ions, and these are called electropositive. In your glass of salty water, chlorine gathers at one wire and hydrogen at the other, and charging a phone sorts the parts of its battery chemicals in just this way.

Splitting compounds by current led to very important discoveries. Many simple substances were first obtained this way. Most famous is the obtaining of potassium and sodium, whose compounds with oxygen Lavoisier and the chemists of his time could not decompose. The Englishman Davy showed that these substances are decomposed by a galvanic current, and at the negative pole he obtained the metals they contain, potassium and sodium. In recent times, when dynamos made current easy to obtain by burning fuel or by water power, Davy's method became convenient and profitable for factories: sodium is

made from molten caustic soda, and chlorine from solutions of table salt. The aluminium in a drinks can is made the same way today, by passing an enormous current through a molten aluminium compound.

The third condition is light. Some unstable compounds are decomposed by light, and photography is based on this property of certain substances, such as silver salts. The mechanical work of the vibrations that make up light is very small, so only some, generally weak, bodies can be decomposed by light, at least under ordinary conditions. But there are chemical phenomena driven by light that are still an unsolved problem of chemistry: those happening in plants. There a great variety of decompositions and combinations takes place, often not yet reproduced by artificial means. Carbon dioxide, so stable against current and heat, is decomposed in plants under the influence of light, giving off oxygen. And chlorine combines with hydrogen not only when heated but also when lit, showing that light can start combinations as well as decompositions. A green plant on your windowsill is quietly doing what no laboratory of Mendeleev's day could: splitting carbon dioxide with nothing but sunlight.



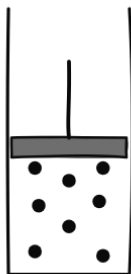
Light splits and joins

The fourth condition is mechanical action, which affects both combinations and decompositions. Many substances decompose from mere friction or a blow, such as nitrogen iodide, a compound of nitrogen, iodine and hydrogen, and the fulminating mercury salt that goes off when struck in percussion caps. Friction makes sulphur burn at the expense of the oxygen in Berthollet's salt. Pressure, together with temperature, sets the state of substances, especially gases: change the pressure and the volume changes greatly, and so does the number of meetings between different particles. So compressed hydrogen acts more strongly on iodine and on solutions of many salts, at suitable temperatures.

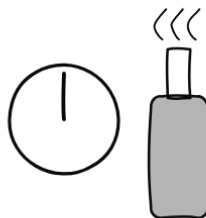
BLOW



PRESSURE



TIME

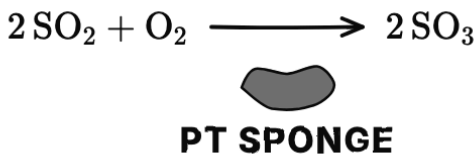
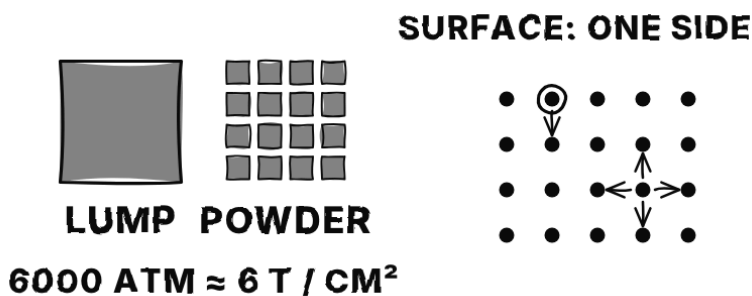


A blow, pressure, time

The fifth condition is time. For bodies to penetrate one another, there must first be mechanical movement, and that goes at a definite speed: a solid burning in air burns at its surface, and depends on that surface being renewed and air flowing in, which takes time. And even after full contact, the inner movement that makes up the reaction needs its own time. The well-known example is the aging of wine, which gives it its bouquet. Fresh wine contains acids and alcohol separately; while it is kept, they react with each other by double decomposition, giving water and fragrant compound ethers. This reaction is slow at ordinary temperature, it is reversible, since the ethers and water can give back alcohol and acid, and its speed depends on temperature and other conditions. There are many such slow reactions, but most of the sharp

chemical changes met at the start of chemistry go so fast that time is usually not taken into account.

The sixth condition is the state of contact between the reacting bodies. Increasing the number of points of contact, other things being equal, increases the intensity of a reaction. Sulphuric acid does not absorb olefiant gas under ordinary contact, but it does with long shaking, because the points of contact grow very greatly in number. Solids, to act on each other fully and quickly, must be mixed as finely as possible, ground to the finest powder.



More contact, faster change

The Belgian chemist Spring showed that powders of solids that do not react at ordinary temperature can be made to react under increased

pressure. At six thousand atmospheres, sulphur combines with many metals at ordinary temperature, and powders of many metals form an alloy. Here is that pressure aloud. One atmosphere presses with roughly one kilogram on every square centimetre, so six thousand atmospheres is about six thousand kilograms, six tonnes, on each square centimetre, like a large lorry standing on a fingertip. The cause here, Mendeleev says, is the increase of points and surfaces of contact, and so solids can react just as liquids and gases do, because in every state of matter the particles keep their inner motion and mobility.

Then comes a subtle point. Inside a substance each particle is acted on by others like it from all sides, but at the surface only from one side. So the state of matter at a surface where it touches other bodies is more or less altered, and may be like the state produced by raising the temperature. This explains the numerous class of contact reactions, which arise from the mere presence, the touch, of certain special bodies, which is called catalysis. Porous and powdery bodies often act this way, above all spongy platinum and charcoal. Sulphur dioxide does not combine directly with oxygen, but in the presence of spongy platinum the combination happens, with heat given off. The catalytic converter under a car does the same job with a film of platinum metals, making exhaust gases react as they pass over it.

These general, introductory ideas of chemistry, Mendeleev ends, get their true meaning only through acquaintance with the particulars of chemistry, to which the book now turns. Yet it was unavoidable to meet from the very start such broad principles as the laws of conservation of matter and of forces, because only by accepting them, and under their guidance, can the study of particulars be practicable and fruitful. So the introduction closes where it began: on the scales, where nothing is lost, and with energy, which only changes its form.

Remember

An electric current acts much like heat but can split even the most stable compounds at ordinary temperature, sending non-metals and acids to the positive pole and metals and hydrogen to the negative one; so Davy first obtained potassium and sodium. Light splits fragile compounds, as in photography, can make chlorine and hydrogen combine, and in plants decomposes even carbon dioxide. Friction, blows and pressure can start reactions, and reactions need time, like the slow forming of wine's bouquet. More points of contact mean a stronger reaction: Spring made powders react at six thousand atmospheres, and surfaces such as spongy platinum set off contact reactions. All the details of chemistry rest on the laws of conservation of matter and of energy, set down at the start.

Questions

1. What advantage does an electric current have over heat for splitting compounds?
 - a. It works at ordinary temperature and can split even the most stable bodies.
 - b. It never produces any combinations.
 - c. It splits only weak compounds, so it is safer.
 - d. It turns compounds into light instead of new substances.

2. When a current splits a compound, where do metals and hydrogen appear?
 - a. At the positive pole, the anode.
 - b. Evenly through the whole liquid.
 - c. At the negative pole, the cathode.
 - d. They do not appear; only non-metals are released.
3. Why does long shaking let sulphuric acid absorb a gas it ignores when they merely touch?
 - a. Shaking warms the acid until it boils.
 - b. Shaking changes the gas into a liquid.
 - c. Shaking frees oxygen from the acid.
 - d. Shaking greatly increases the number of points of contact.
4. Why can the surface of a body such as spongy platinum set off a reaction?
 - a. Because platinum gives its own substance to the products.
 - b. Because particles at a surface are acted on from one side only, so their state is altered, rather as if heated.
 - c. Because platinum always carries an electric current.
 - d. Because light is focused at the surface of porous bodies.

Answers

1. **a)** Current acts much like heat, but the splitting can be done more conveniently at ordinary temperature, and even the most stable bodies give way.
2. **c)** Metals, hydrogen and similar products appear at the negative pole and are called electropositive; non-metals and acids go to the positive pole.

3. d) More points of contact, other things being equal, mean a more intense reaction, and shaking multiplies them.

4. b) Inside a body each particle is pulled from all sides, at the surface from one; the altered state there can be like that of a higher temperature, which explains contact reactions.

Worked examples

How hard Spring pressed Spring made sulphur combine with metals at ordinary temperature under 6000 atmospheres. Taking one atmosphere as roughly one kilogram on each square centimetre, what load is that on a square centimetre?

Each atmosphere is roughly one kilogram on every square centimetre.

6000 atmospheres is therefore 6000 times one kilogram on each square centimetre.

That is 6000 kilograms, or six tonnes, on each square centimetre.

Such a pressure crowds the surfaces of the powders together, multiplying the points of contact so they can react.

Answer: About 6000 kilograms, six tonnes, on each square centimetre

Practice

1. At how many atmospheres would a powder be pressed with about one and a half tonnes on each square centimetre?

Hint: One atmosphere is roughly one kilogram on a square centimetre; a tonne is a thousand kilograms.

Answer: About 1500 atmospheres. One and a half tonnes is 1500 kilograms, and at roughly one kilogram per atmosphere that is 1500 atmospheres, a quarter of Spring's 6000.

2. Why could Davy obtain potassium and sodium when Lavoisier could not?

Hint: What can a current do that heat and the methods of Lavoisier's day could not?

Answer: The compounds of potassium and sodium with oxygen were too stable for the means of Lavoisier's time. Davy passed a galvanic current through them, which splits even the most stable compounds, and the metals appeared at the negative pole.

3. Explain why aging wine slowly gains its bouquet, using the idea that reactions need time.

Hint: What reacts in the wine, and how fast at ordinary temperature?

Answer: Fresh wine holds acids and alcohol separately. While it is kept, they react by double decomposition into water and fragrant compound ethers, but at ordinary temperature this reversible reaction runs slowly, at a limited speed, so the bouquet appears only over time.