

The Principles of Chemistry



Dmitri Mendeleev · 1903

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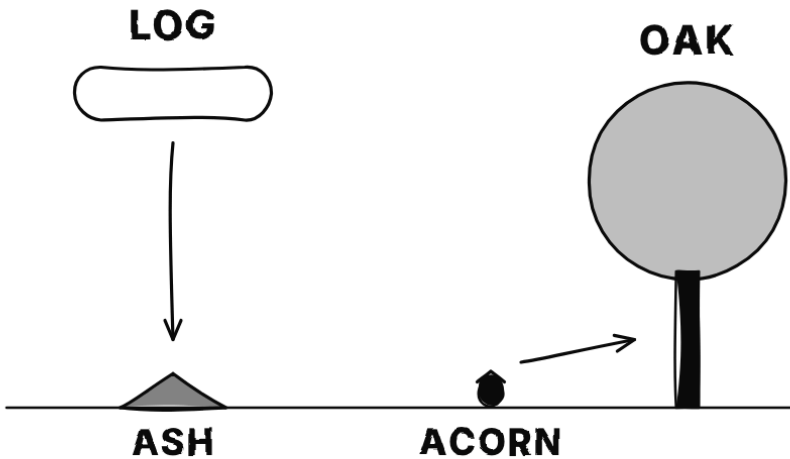
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Where Does the Log Go?

Put a log on a campfire and come back an hour later. Where the heavy log lay, there is only a little heap of grey ash. Now think of an acorn, light enough to blow off your hand, that becomes, many years later, an oak heavier than a car. In the fire, matter seems to vanish; in the tree, it seems to appear from nowhere. Mendeleev begins his great book on chemistry by showing that both impressions deceive us, and that seeing through them is what turned chemistry into a science.

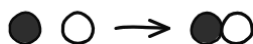
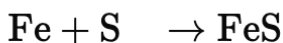


Lost in fire, made in a tree?

What does chemistry study? In Mendeleev's words, its nearest subject is the uniform substances from which all the bodies of the world are made, the ways they turn into one another, and what happens while they do. Such a change is called a reaction. A reaction needs the closest possible contact: the substances must truly touch, down to their smallest invisible particles, which Mendeleev calls molecules. Physics already knew gravity, cohesion, heat, light and electricity. Chemistry had to add something new: forces hidden inside those tiny particles, silent in everyday life, but plainly at work whenever one substance becomes another.

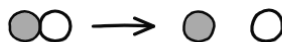
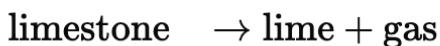
Mendeleev names three main kinds of reaction. The first is combination, where two substances become one. Mix iron filings and yellow sulphur powder: a magnet can still pull the iron out, so this is only a mixture. Heat it, and the mixture glows and turns into a dark new substance, iron sulphide, where no magnifier can find either iron or sulphur any more. Combinations usually give off heat, and ordinary burning is one of them: the fuel joins with a part of the air called oxygen. The blue flame under your kettle is this kind of reaction, gas joining oxygen and giving out the heat that boils the water.

COMBINATION



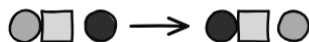
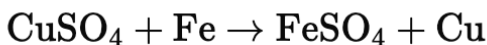
IRON + SULPHUR → IRON SULPHIDE

DECOMPOSITION



THE GAS IS CARBON DIOXIDE

SUBSTITUTION



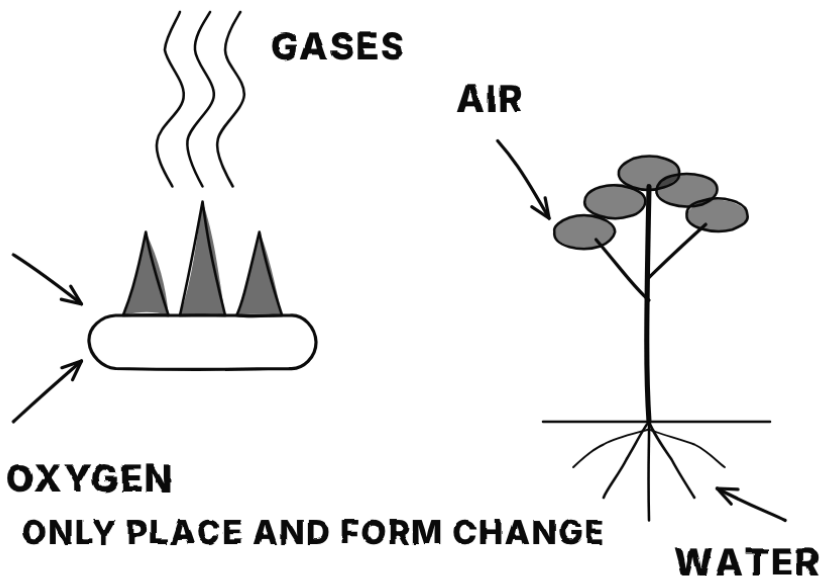
Three kinds of reaction

The second kind is decomposition, the reverse: one substance falls apart into several. Heat wood strongly with no air getting in, and it gives a gas that burns, a watery liquid, tar and charcoal; factories once made charcoal and lighting gas exactly this way. Limestone, chalk and marble, heated strongly, leave lime behind and give off a gas, carbon dioxide. Decompositions usually take in heat rather than give it out. A cement factory's kiln must burn fuel day and night, because splitting limestone into lime and gas costs heat.

The third kind lies in between: as many substances come out as went in, because one part changes places with another. Dip an iron nail into a blue solution of copper vitriol. Soon the nail is coated in red copper, and the solution turns green, because iron has taken copper's place in

the salt. Mendeleev calls this substitution, and says such reactions are used all the time to coat iron with copper, or copper with silver. A silver-plated spoon owes its shine to the same idea: one metal set down on another out of a solution.

If people had used such changes for thousands of years, why did a real science of them come so late? Mendeleev gives two reasons. First, most changes in nature and in workshops are tangled: many combinations, decompositions and substitutions happen at once. Second, and more important, gases take part in a great many reactions, above all the air itself. Only in the sixteenth and seventeenth centuries did people grasp that air has weight, and that a gas is a springy state of matter spreading out in every direction. Until then, gases went in and out of reactions unseen and unweighed, so it looked as if matter could be made and unmade.

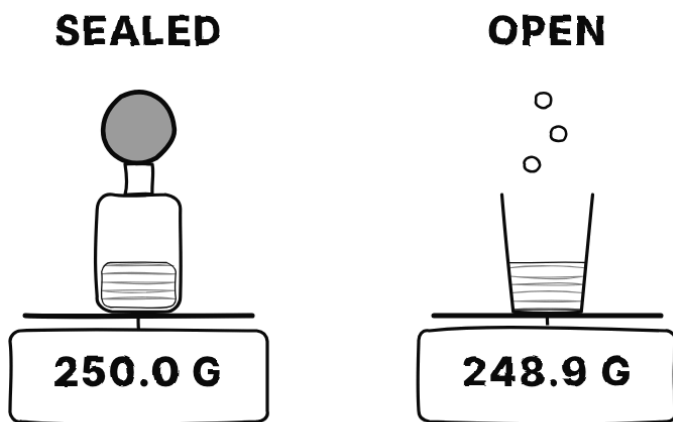


Where the burned log goes

Look again at the campfire. The wood does not vanish: it turns into gases that leave as smoke. Catch that smoke and you find gases unlike air, in which a candle goes out and an animal cannot breathe. Weigh them, and they weigh more than the wood, because the wood has joined with part of the air, just as iron grows heavier when it rusts. The acorn, too, does not grow out of itself: its leaves take in gases from the air and its roots draw up water with what is dissolved in it, and from these the tree builds its body. In a gas without the nourishing part of the air, a plant does not grow at all; it dies. Even water drying from a wet shirt is not lost; it comes back as rain, dew or snow. Matter, through every change, only changes its place and its form, and keeps its amount. In Mendeleev's own short phrase, matter is eternal for us.

Try it yourself

Put a bottle with a little vinegar and a small paper twist of baking soda on a kitchen scale, and stretch a balloon over the neck. Note the reading, then tip the soda in by shaking the bottle without lifting it. It fizzes and the balloon swells, yet the number on the scale stays where it was. Do the same in an open glass and the reading creeps down as the gas escapes. Your kitchen scale shows in a minute what took chemists centuries: the lost weight was only gas let go.



WEIGHT IN = WEIGHT OUT

Sealed bottle, open glass

A few ancient Greek thinkers, and seventeenth-century scientists such as Mariotte, already suspected that the amount of matter never changes, but they never stated it clearly or used it. The proof came in the second half of the eighteenth century from Antoine Lavoisier, a French academician who also collected taxes, and whom Mendeleev calls the founder of modern chemistry. His instrument was the balance, the only tool that tells directly and precisely how much of a substance there is. He weighed everything he started with, even the vessels, and then weighed everything that came out. Every time, the products together weighed exactly as much as the starting substances together.

This is the law of conservation of matter: matter is neither created nor destroyed. Mendeleev adds an honest remark. Such a short sentence speaks for all of nature, so it holds a guess; what has actually been seen is more modest. In all experiments and all phenomena studied, nobody has ever found the products heavier or lighter than what was taken, as far as the scales can tell. And since weight goes hand in hand with the amount of matter, nobody has ever seen matter disappear or new matter appear. That modest, careful finding is what gives every chemical investigation its precision, because it lets the chemist keep an exact account of every reaction. Today's laboratory scales can show a ten-thousandth of a gram, and the account still balances.

Remember

Chemistry studies how substances turn into one another, and every such change, a reaction, needs the closest contact between their tiny particles. Reactions come in three main kinds: combination, where substances join; decomposition, where one falls apart; and substitution, where one part takes another's place. The science came late because reactions are tangled and because invisible gases, which do have weight, were left out of the picture. Lavoisier weighed everything before and after, and found the total never changes: matter is neither made nor lost, only moved and transformed.

Questions

1. The gases from a burned log weigh more than the log did. Where does the extra weight come from?
 - a. From the heat of the fire, which turns into a little matter.
 - b. From the ash, which hands some of its weight to the smoke.
 - c. From the air, because the wood joins with a part of it as it burns.
 - d. From the moisture of the wood, which grows heavier when heated.
2. A sealed bottle of vinegar and baking soda sits on a kitchen scale. The two fizz together and the balloon swells. What does the scale show?

- a. The same reading as before, because nothing left the bottle.
 - b. A lower reading, because the gas weighs nothing.
 - c. A higher reading, because a new substance was made.
 - d. A lower reading, because the fizzing uses up some matter.
3. Why was it so hard for early chemists to see that matter is never lost?
- a. They had no scales of any kind.
 - b. They did not know that air and other gases have weight, so gases went in and out of reactions unnoticed.
 - c. Reactions in their time happened more slowly than today.
 - d. They believed only in combinations and never saw a decomposition.
4. An iron nail in blue copper vitriol becomes coated with copper and the solution turns green. What kind of reaction is it?
- a. A combination, because copper joins the nail.
 - b. A decomposition, because the blue salt simply falls apart.
 - c. A melting of the nail into the solution.
 - d. A substitution, because iron takes copper's place in the salt.

Answers

- 1. c)** The wood combines with part of the air, just as iron grows heavier when it rusts, so the gases carry the wood's weight plus the air's.
- 2. a)** The gas is caught in the balloon, so all the matter is still on the scale; only in an open glass does the reading drop as the gas escapes.
- 3. b)** Until people grasped that air has weight, gases went in and out of reactions unseen and unweighed, so matter seemed to appear and vanish.

4. d) As many substances come out as went in, because iron has changed places with copper: that is substitution.

Practice

1. A friend says that a growing tree proves matter can be created, since an acorn becomes a huge oak. How would you answer?

Hint: Ask what the leaves and the roots take in.

Answer: The tree builds its body from what it takes in: gases from the air through its leaves, and water with dissolved substances through its roots. Its weight comes from outside; nothing is created. Without the nourishing part of the air a plant does not grow at all.

2. Iron filings and sulphur are mixed, then heated until they glow. How could you show that before heating it was only a mixture, and afterwards a new substance?

Hint: Think of what a magnet does in each case.

Answer: Before heating, a magnet pulls the iron out of the mixture, so the two are still separate. After heating, the magnet can no longer pick out iron and no magnifier shows either iron or sulphur: they have combined into one new substance, iron sulphide.

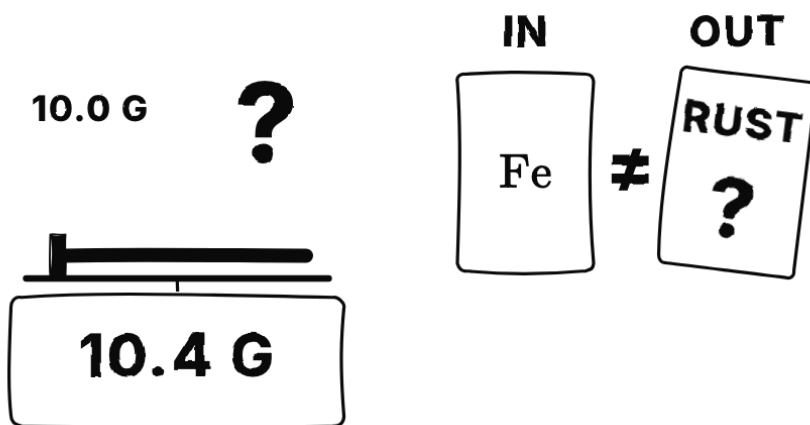
3. A wet shirt hung out to dry becomes lighter. Has some of its matter been destroyed? Explain.

Hint: Follow the water after it leaves the shirt.

Answer: No. The water has only changed its place and form: it went into the air as vapour and comes back later as rain, dew or snow. The shirt is lighter, but the total amount of matter is the same.

The Scales as a Detective

Leave a shiny iron nail outside in the damp for a week. It turns brown and flaky, and if you had weighed it first, you would find it is now heavier. Something has joined it, yet nothing visible came near. The rule from the last part, that nothing is made or lost, is about to work like a detective and name the culprit.

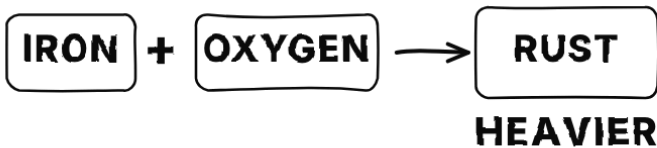


The rusty nail weighs more

Mendeleev turns the rule into a balance sheet. On one side stand all the substances that go into a reaction, on the other all that come out, and the two sides must weigh the same. That gives the chemist two

powers. If every weight but one is known, the missing one can be found. And if a substance has been forgotten, the two sides will not match, and that mismatch gives the omission away. It works like a shop's till at closing time: if the cash and the receipts do not agree, something was missed, and you go looking for it.

The first case is iron. In damp air it rusts, and heated in air it grows a crust of scale, an earthy stuff much like the iron ores dug out of the ground. Either way the metal gains weight. Lavoisier found where the extra comes from: the part of the air called oxygen, the part that keeps fires burning. In empty space, or in gases with no oxygen such as hydrogen or nitrogen, iron neither rusts nor scales. So rust is iron plus something, a combination, and more complex than the iron itself.



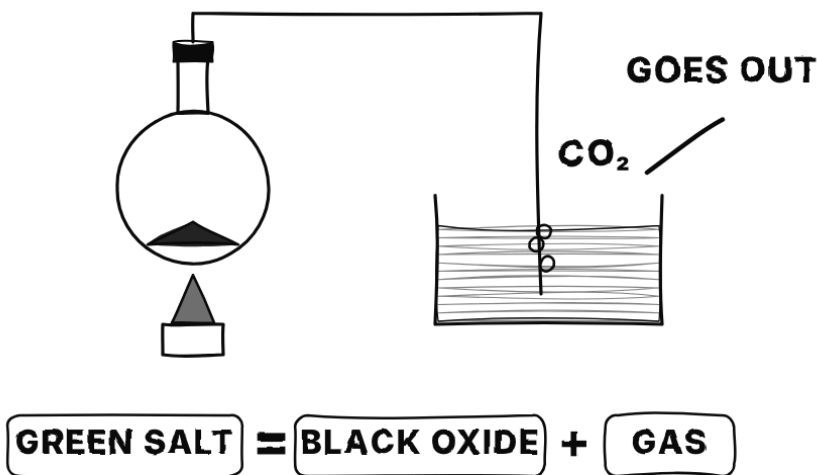
NO OXYGEN: NO RUST



Iron gains, it does not lose

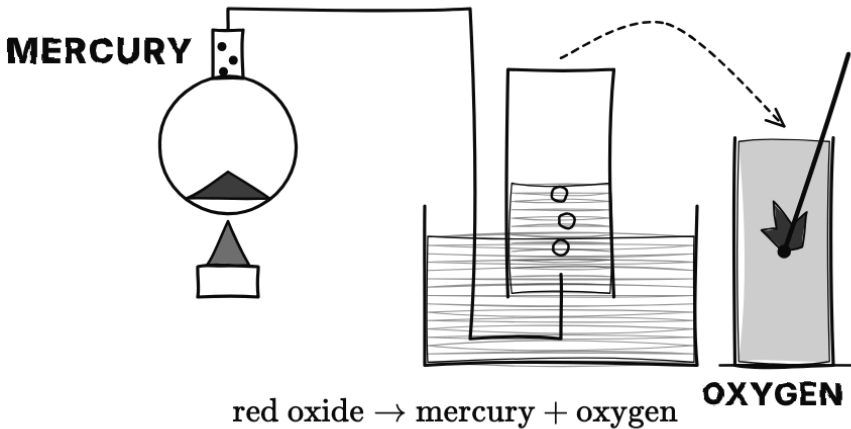
Without weighing, it is easy to read this backwards, and before Lavoisier everyone did. Chemists then believed that iron held a mysterious substance called phlogiston, and that heating drove it out and left the scale behind. But something leaving would make the scale lighter, and it is heavier. The scales alone were enough to overturn the old idea. The rust that eats an old bicycle is heavier than the steel it replaces, because it has taken oxygen from the air.

The second case goes the other way. The green copper salt sold as a powder, and the green stone malachite, used in jewellery and as a copper ore, turn black when heated. The black stuff, copper oxide, weighs less than the green salt, so this time something has left: it is a decomposition. Fit the flask with a tight stopper and a tube leading into water, and bubbles of gas come out as it heats. A burning splinter goes out in this gas as if dipped in water. It is carbon dioxide, clear and colourless like air, which is exactly why, without scales, nobody would have suspected it was there. Weigh it too, and the black oxide and the gas together weigh just what the green salt did.



Green salt gives off a gas

The third case is the one Mendeleev calls especially important for the history of chemistry. Mercury heated in air slowly turns into a red powder, red mercury oxide. Heat that red powder in a glass flask whose tube dips under water, and catch the bubbles in an upturned jar full of water, which they push down as they rise. The first bubbles are just air, expanding in the heat; then comes a different gas. Lower a splinter that is only glowing into it, and the splinter bursts into a bright flame, which in ordinary air it would never do. That gas is oxygen. At the same time, a shiny film and tiny droplets of mercury collect on the cooler glass. So one substance has split into two, mercury and oxygen, a decomposition.



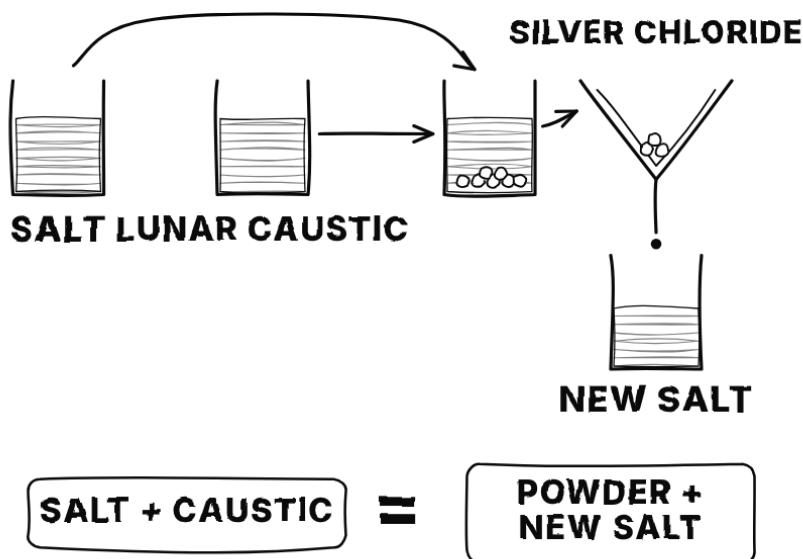
Red powder splits in two

Chemists before Lavoisier could already collect gases, but he showed what they actually do. The oxygen from the red powder is the same gas that is in the air, that animals breathe, that things burn in, and that turns metals into rust and scale. That is why such a small experiment changed the whole of chemistry.

Try it yourself

Blow out a match and, while the tip still glows, hold it just above a glass of pharmacy hydrogen peroxide into which you have stirred a pinch of dried yeast. The foam is full of oxygen, and the glowing tip brightens or even flares up again. It is Mendeleev's glowing-splinter test, done in a kitchen glass instead of a laboratory flask.

The fourth case shows a substitution. Take table salt, and lunar caustic, the silver salt once used to cauterise wounds. Both dissolve in water into clear solutions. Pour the two together, and at once a white solid appears and sinks: a new substance that will not dissolve. Pour the cloudy mixture into a glass funnel lined with a cone of unsized paper, a filter, and the clear liquid runs through while the white powder stays on the paper. That powder, silver chloride, is plainly a new substance, since neither starting salt was insoluble. Boil the clear liquid dry, and it leaves another new salt, soluble in water but different from both of the first two. The water only served to bring the two salts into a loose, liquid state where they could meet. Mendeleev dried and weighed everything: the salt and the lunar caustic taken together weighed exactly as much as the white powder and the new salt together. A coffee filter in your kitchen does the same job as Mendeleev's paper cone, keeping the solid and letting the liquid through.



Two salts swap partners

Remember

Because nothing is made or lost, the weights going into a reaction must equal the weights coming out. That balance sheet lets a chemist work out one unknown weight, and it exposes any substance that was overlooked, like an invisible gas. Rusting iron gets heavier because it takes oxygen from the air, which disproved the old idea of phlogiston escaping. Green copper salt gets lighter on heating because it gives off carbon dioxide, and red mercury oxide splits into mercury and oxygen, the gas of breathing and burning. Salt and lunar caustic exchange partners in water, and still the total weight stays exactly the same.

Questions

1. A chemist adds up the weights before and after a reaction, and the two totals do not match. What is the most sensible conclusion?
 - a. Some matter was destroyed during the reaction.
 - b. Some substance that took part was left out of the account.
 - c. Some matter was created by the heat.
 - d. The balance sheet works only for reactions without gases.
2. Why did the weighing of rust overturn the old idea of phlogiston?
 - a. Because rust turned out to be lighter than the iron.
 - b. Because phlogiston was found in the air instead of in iron.
 - c. Because rust is heavier than the iron, so something was added, not driven out.
 - d. Because iron rusted just as well in a vessel with no air.
3. Green copper salt turns black and gets lighter when heated. What has happened?
 - a. It has given off a colourless gas, carbon dioxide, and the rest is black copper oxide.
 - b. It has taken oxygen from the air and become copper oxide.
 - c. Part of its matter has burned away into nothing.
 - d. It has melted and lost its water of colour.
4. Table salt and lunar caustic solutions are mixed and a white powder settles. Why is this a substitution and not just a

mixture?

- a. Because the water has turned into a new salt.
- b. Because the powder is only the two salts dried out of the water.
- c. Because the mixture grew heavier than the two salts.
- d. Because two new substances appear, one insoluble and one soluble, unlike either salt taken.

Answers

- 1. **b)** Since nothing is made or lost, a mismatch means something was forgotten, often an invisible gas, and the mismatch itself gives it away.
- 2. **c)** If phlogiston left the iron, the rust would weigh less; it weighs more, because the iron has taken oxygen from the air.
- 3. **a)** Losing weight means something left; the stoppered flask shows bubbles of carbon dioxide, and oxide plus gas weigh just what the salt did.
- 4. **d)** Two substances have given two new ones, the insoluble silver chloride and a new soluble salt, while the water only helped them meet.

Worked examples

Mendeleev's own weighing Mendeleev takes about $58\frac{1}{2}$ grams of table salt and 170 grams of lunar caustic, and gets $143\frac{1}{2}$ grams of insoluble silver chloride and 85 grams of a new soluble salt. Does this agree with the rule that nothing is made or lost?

On the going-in side stand the two salts taken: $58\frac{1}{2}$ and 170 grams, together $228\frac{1}{2}$ grams.

On the coming-out side stand the two new substances: $143\frac{1}{2}$ and 85 grams, together also $228\frac{1}{2}$ grams.

The water is left out on both sides, because it only brought the salts together and was not used up.

The two sides are equal, just as the rule demands.

Answer: Yes: both sides weigh $228\frac{1}{2}$ grams.

Practice

1. Someone weighs a dish of green copper salt, heats it in the open, and finds the black powder lighter. They say heat destroys matter. What would you tell them?

Hint: Ask what could have left the dish without being seen.

Answer: Nothing was destroyed: a colourless gas, carbon dioxide, escaped. Heating in a stoppered flask with a tube into water shows the bubbles, and the black oxide and the gas together weigh as much as the salt did.

2. Iron is heated in a vessel of nitrogen instead of air, and no scale forms and the iron gains no weight. What does this show?

Hint: Compare with ordinary air, which contains oxygen.

Answer: It shows that the extra weight of scale comes from the oxygen in the air: where there is no oxygen, nothing joins the iron, so nothing is added.

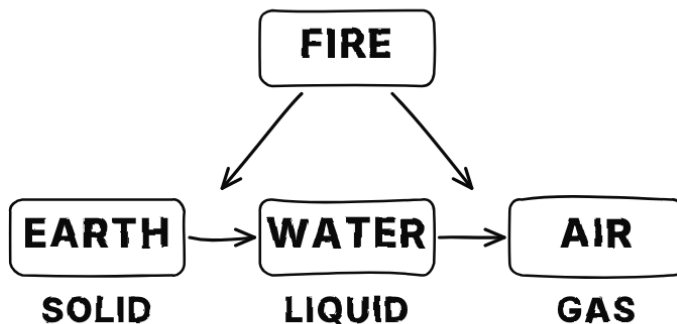
3. A glowing splinter is lowered into a jar of gas from heated red mercury oxide and bursts into flame. Why does this prove the gas is not just air?

Hint: What does a glowing splinter do in ordinary air?

Answer: In ordinary air a merely glowing splinter dies by itself. Bursting into flame shows the gas keeps burning going far more strongly than air: it is oxygen, set free from the red powder.

Twelve Days with a Flask of Mercury

Can you make anything out of anything? Watch a plant build leaves, wood and fruit out of nothing but air, water and soil, and it seems there is no end to what matter can become. Watch a blacksmith turn iron into ink or into the deep blue paint called Prussian blue, and the feeling grows. And yet every one of us knows you cannot cook a meal out of a stone, or turn copper into gold. Mendeleev calls this the second great question of chemistry. The first was about quantity, and the scales answered it: nothing is lost. The second is about quality: is there a limit to what a substance can be turned into?



NO LIMIT?

The four old elements

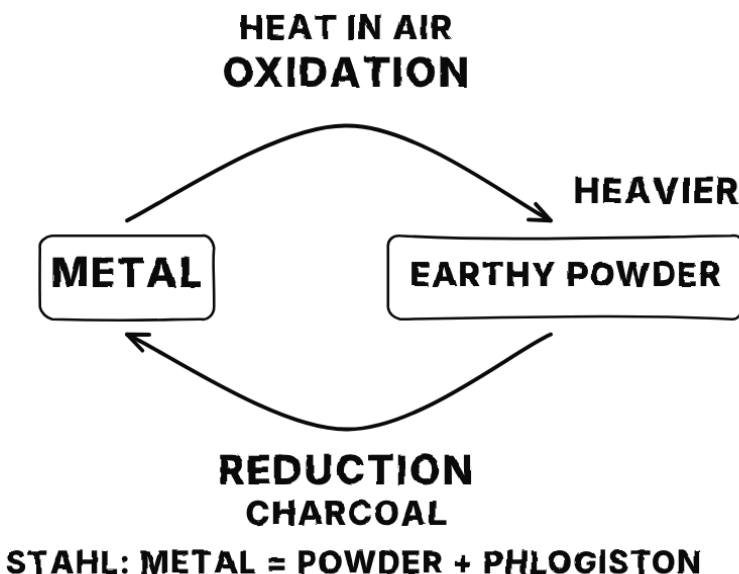
The oldest popular answer said that everything is made of four elements: air, water, earth and fire. It came from Asia to the Greeks, and Empedocles set it out most fully, some four and a half centuries before Christ. It was not the fruit of careful research; it seems simply to sort things into gases, liquids and solids, with fire, that is heat, changing one into another.

Arab scholars were the first to attack the question by experiment, and through Spain they brought this passion to Europe, where it became the secretive art of alchemy. The alchemists believed that change has no limit, and they hunted for the philosopher's stone, a substance that would turn anything into gold and diamonds and even make the old young. Their belief was not mere fancy. From a shiny ore called galena they got lead, and from lead they got silver, so it seemed that one more step would lead from silver to gold. They rarely weighed, though. Had they done so, they would have seen that the silver was a tiny part of the lead, and that once taken out, no further work would give any more. The silver had been sitting in the lead all along; the lead had not turned into it. It is like finding coins in an old sofa: the sofa did not make them, and shaking it again gives nothing. The alchemists found no laws, because they never asked simple, clear questions, but they left chemistry a treasure of experiments.



The silver was already there

Two of their favourite changes turned out to be the key to everything. When a metal rusts, or more generally passes from shiny metal into an earthy powder, we call it oxidation. 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 come back as metal when heated with charcoal. Many ores in the ground are exactly such oxidised metals, and furnaces have always won tin, iron and copper from them by heating them with charcoal. A blast furnace at a steelworks is still doing just this: ore and coke go in at the top, iron runs out at the bottom.



Oxidation and reduction

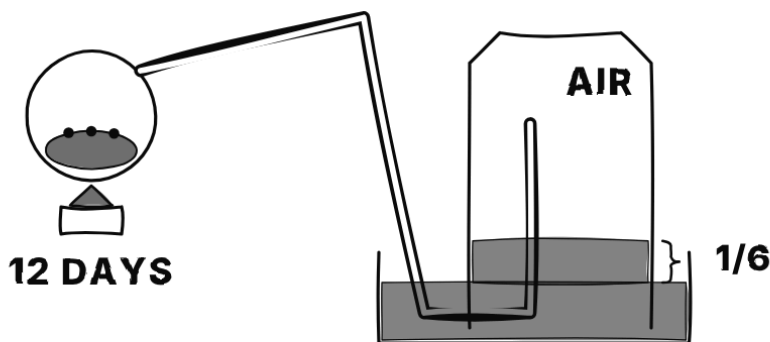
The first explanation of these two changes came from Becher and above all from Stahl, physician to the King of Prussia, in a book of seventeen twenty-three. Every body, Stahl said, holds a weightless fiery substance he called phlogiston. The more easily a body burns or rusts, the more phlogiston it has, and charcoal is full of it. When a metal rusts or burns, the phlogiston leaves; when charcoal turns an ore back into metal, it hands the ore some of its own phlogiston. So, for Stahl, a metal was a compound: earthy powder plus phlogiston. The theory was so simple that it won a great many admirers.

Lavoisier, with his scales, saw that every rusting and every burning makes the substance heavier, at the expense of the air. He took the natural view that the heavier body is the more complex one, and in

seventeen seventy-four he made the famous experiment that settled the matter.

Picture a glass flask with a long neck that bends down and then up again. Lavoisier poured pure mercury into it, ran the neck into a dish of mercury, and covered the open end with a glass bell full of air. So a fixed amount of air was trapped, cut off from the room. He measured that air carefully beforehand, taking into account the size of the flask and bell, the mercury inside, and the temperature and pressure of the day. This was the whole point: if Stahl was right, phlogiston would pour out of the mercury into the air, and the air ought not to shrink; if Lavoisier was right, the mercury would swallow part of the air, and the air would shrink.

AIR LOST = MERCURY GAINED



Twelve days of hot mercury

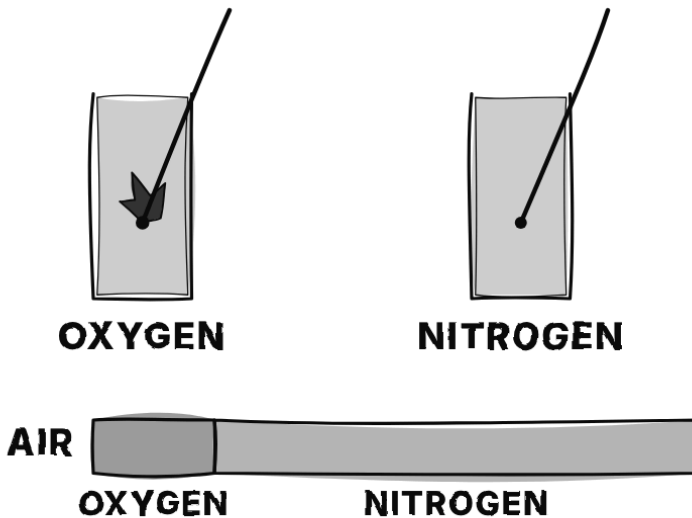
For twelve days he kept the mercury hot, almost boiling. Little by little its surface became covered with red scales: the red mercury oxide we met in the last part. Then he let the apparatus cool and measured the air again. It had shrunk, by about a sixth, and that alone refuted the German theory. Better still, the air had lost exactly as much weight as the mercury had gained. So part of the air had not vanished; it had joined the mercury.

Try it yourself

Push a pad of damp steel wool into the bottom of a tall glass and stand the glass upside down in a saucer of water. Over a day or two the wool rusts, and the water climbs about a fifth of the way up inside the glass. Your saucer is a rough kitchen version of Lavoisier's bell: the iron has taken part of the trapped air into its rust, and what is left will not keep a flame alight.

That swallowed part of the air can be driven back out of the red oxide, and it is the gas in which a glowing splinter blazes up. It was named oxygen. The part of the air left under the bell behaved quite differently. It would not rust metals and could keep neither a flame nor a living creature going; a burning splinter, Lavoisier wrote in his report, "goes out in it as if plunged into water". This gas was named nitrogen.

RUST = METAL + OXYGEN



Air is two gases

So air is not an element at all, as the ancients thought, but a mixture of two gases, oxygen and nitrogen. Mix them back together, and you get ordinary air once more. Burning and rusting take oxygen out of the air, and the earthy powders that metals turn into are compounds of metal and oxygen. And when charcoal turns an ore back into metal, the oxygen leaves the ore and joins the charcoal, making the same gas that charcoal makes when it burns in air. That gas too is a compound, of charcoal and oxygen, just as the earthy powders are of metal and oxygen. Stahl had the story exactly backwards: the metal is the simpler body, and its rust is the metal plus something.

Remember

After asking how much matter there is, chemistry asks what it can become: is there a limit to transformation? The alchemists thought there was none, but their silver had always been in the lead, as weighing would have shown. Oxidation turns a metal into an earthy powder, and reduction with charcoal brings the metal back; Stahl explained both with an imagined phlogiston. Lavoisier heated mercury under a bell of air for twelve days, and the air shrank by as much weight as the mercury gained. Air is a mixture of oxygen, which joins metals and keeps fires burning, and nitrogen, which does neither; rust is metal plus oxygen.

Questions

1. The alchemists got silver out of lead. Why did this not prove that lead can turn into silver?
 - a. Because the silver they got was really polished lead.
 - b. Because the silver was already in the lead, and once taken out no more could be got.
 - c. Because silver can only be made from galena, never from lead.
 - d. Because the lead turned into silver only while it was hot.
2. In Lavoisier's twelve-day experiment, the trapped air shrank while the mercury grew red scales. Why did this count against Stahl's phlogiston?

- a. Stahl expected phlogiston to pour out into the air, so the air should not have shrunk.
 - b. Stahl expected the mercury to stay shiny, and it turned red.
 - c. Stahl expected the experiment to take less than twelve days.
 - d. Stahl expected the mercury to boil away completely.
3. What did the gas left under Lavoisier's bell, after the mercury had taken its share, turn out to be like?
- a. It made a glowing splinter burst into flame.
 - b. It was exactly the same as ordinary air.
 - c. It would neither rust metals nor keep a flame or a creature alive.
 - d. It turned the mercury back from red to shiny.
4. When an ore is heated with charcoal and gives back its metal, where does the ore's oxygen go?
- a. It stays in the metal as phlogiston.
 - b. It is destroyed by the heat of the furnace.
 - c. It becomes nitrogen and escapes into the air.
 - d. It joins the charcoal, making the same gas that burning charcoal makes in air.

Answers

1. **b)** Weighing and closer study would have shown that the silver was a tiny part already sitting in the lead; the lead itself had not turned into anything.
2. **a)** If something left the mercury, the air would not lose anything; instead the air shrank by as much weight as the mercury gained, so part of the air had joined the metal.

- 3. c)** The leftover gas, nitrogen, could keep neither burning nor breathing going; the part that joined the mercury was oxygen.
- 4. d)** In reduction the oxygen passes from the ore to the charcoal, forming the gas of burning charcoal, itself a compound of charcoal and oxygen.

Practice

1. Explain in your own words why Stahl's theory and Lavoisier's view predict opposite things for the air in a closed vessel where a metal rusts.

Hint: Ask, for each of them, whether something goes into the air or comes out of it.

Answer: For Stahl, rusting drives phlogiston out of the metal, so nothing is taken from the air and it should not shrink. For Lavoisier, the metal takes part of the air into itself, so the air should shrink. Lavoisier's mercury experiment showed the air shrinking, by as much weight as the metal gained.

2. The ancients counted air as one of the four elements. What did Lavoisier's experiment show about this?

Hint: Think about the two different gases that came out of the experiment.

Answer: Air is not a single simple thing but a mixture of two gases: oxygen, which joins metals and keeps fires burning, and nitrogen, which does neither. Mixing them back together gives ordinary air again.

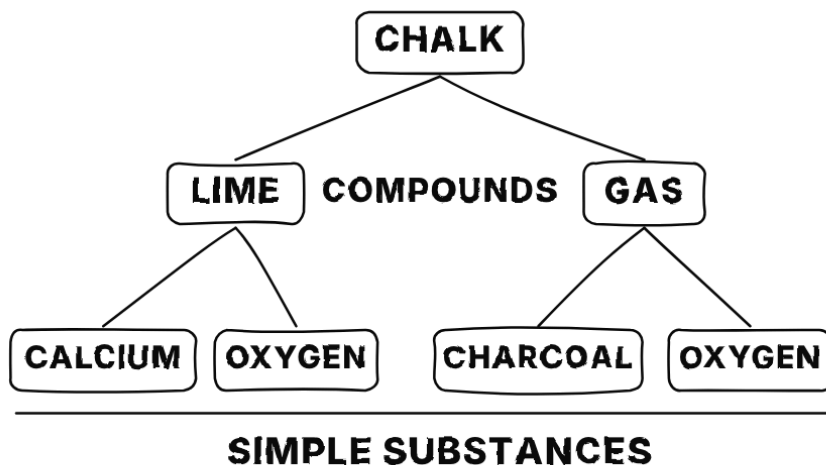
3. Why did the alchemists, for all their skill, find no laws of chemistry?

Hint: Think of what they rarely did, and of the kind of questions they asked.

Answer: They rarely weighed, so they could not see that silver was only taken out of lead, not made from it, and they did not ask simple, clear questions whose answers would let them go further. Still, their many experiments left chemistry a wealth of new facts.

The Bricks That Never Change

Heat a piece of chalk strongly, and it falls apart into quicklime and a gas, the same gas that charcoal makes when it burns. Now let that lime stand in the gas with a little water, at ordinary temperature, and you get back a stony substance just like chalk. So chalk is not a basic stuff at all: it can be taken apart and put together again. But are its two parts basic? Not either: the gas is charcoal joined with oxygen, and lime is a special metal, calcium, joined with oxygen. Mendeleev's question is simple: if we keep taking things apart like this, where do we stop?



Taking chalk apart

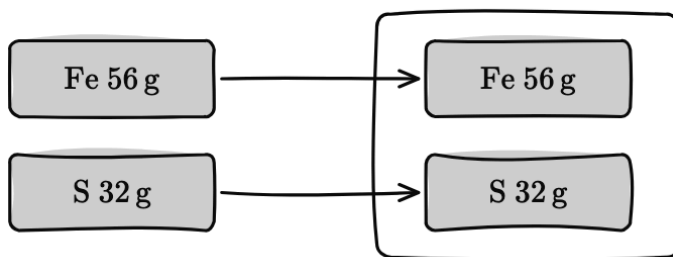
We stop at substances that no means whatever can split into two or more others, and that cannot be built out of anything else either. They can only join with each other, or act on other bodies. Mendeleev calls these simple substances, and everything else compound substances. This division of all uniform substances into simple and compound goes back to Lavoisier and has stayed in science ever since. Think of a house of Lego: you can pull it apart into walls, the walls into bricks, but the single brick is where the pulling stops.

There are remarkably few simple substances compared with the endless compounds they make. In Mendeleev's day about seventy-five were known for certain, and several of them are rare or found only in tiny amounts. The ones whose compounds we deal with in daily life number no more than about twenty-five.

≈ 75 SIMPLE SUBSTANCES ABOUT 25 IN DAILY LIFE

BEFORE

after: FeS



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

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

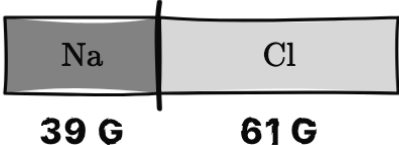
Each simple substance balances

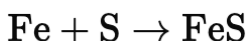
And here is the answer to the alchemists' dream. Simple substances do not turn into one another; nobody has ever seen it happen. In spite of enormous effort, no fact has been found that would suggest that well-known simple substances like oxygen, iron or sulphur are themselves made of anything simpler. So one metal cannot be turned into another.

Put this together with the rule that nothing is made or lost, and something stronger follows. Since a simple substance can be neither made nor broken down, the amount of each one stays the same through every chemical change. It is no longer only the total weight that balances: each simple substance balances on its own. Whatever iron, oxygen or sulphur is in the substances you start with is exactly

what will be found, shared out differently, in the substances you end with. So, Mendeleev says, the heart of chemistry is to find out what each simple substance is joined to, and how, before a change and after it. A bank works the same way: money moves from account to account, but every pound can be traced, and the total in each currency never changes.

To write such changes down briefly, chemists agreed on a shorthand. Each simple substance gets one or two letters from its Latin name: oxygen from oxygenium, nitrogen from nitrogenium, mercury from hydrargyrum, iron from ferrum. A compound is written by placing the letters of its simple substances side by side, so the red mercury oxide is written with the letters for mercury and oxygen together. Each letter also stands for a definite relative weight of that simple substance, its atomic weight. So a written formula tells you not only what a compound is made of, but how much of each is in it. For table salt, made of sodium and chlorine, the formula shows that out of every hundred grams, roughly two fifths is sodium and three fifths is chlorine. And every chemical change can be written as a kind of equation, where the amount of each simple substance must come out the same on both sides.

O	OXYGENIUM	HgO
N	NITROGENIUM	RED MERCURY OXIDE
Hg	HYDRARGYRUM	NaCl
Fe	FERRUM	



Letters from Latin names

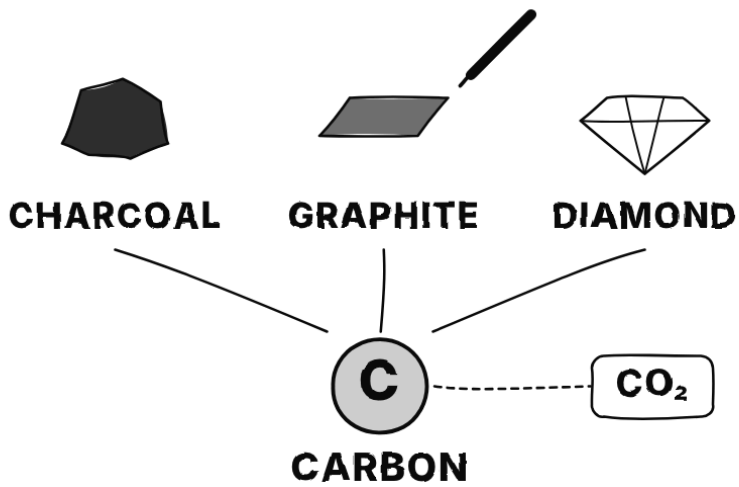
This puts a first limit on chemical change: from given substances you can get only those that contain the very same simple substances. Yet even within that limit, the number of possible compounds is boundless. Anyone starting work in a laboratory can easily make a new compound nobody has made before, and science often foresees such new compounds in advance. Chemistry's aim is to find the order hidden in this huge variety, the laws that govern how compounds form and what properties they have.

Now comes a fine but important distinction. When we say that red mercury oxide contains oxygen, we do not mean that oxygen gas is sitting inside the red powder. We only mean what the powder can do: that it can give up mercury and oxygen, and hand them over to other

bodies. In short, the composition of a compound describes the changes it is capable of. So the red oxide contains not two simple substances, a liquid metal and a gas, but two elements, the stuff of mercury and the stuff of oxygen. It is, Mendeleev says, like steam, which contains the substance of ice but not ice itself, or bread, which contains the substance of grain but not the grain. Your kitchen sugar works the same way: it holds the element carbon, but there is no lump of charcoal hidden in the sugar bowl.

An element can even be known before anyone has seen its simple substance. For a long time nobody had obtained fluorine on its own, yet it had to be counted an element, because its compounds with other substances were known and were plainly unlike any others.

The difference shows most clearly in carbon. Charcoal, graphite and diamond are three different simple substances: one black and crumbly, one grey and slippery, one clear and the hardest of all. Yet all three are the same element, carbon. That same carbon is in the gas made by burning charcoal, and yet that gas holds neither charcoal, nor graphite, nor diamond. A simple substance can come in several forms; the element is what stays unchanged beneath them all. The pencil lead in your drawer and the stone in a diamond ring are, deep down, the same element.



Three bodies, one carbon

Remember

Taking substances apart, we reach simple substances, which can be neither split nor built from anything else; all others are compounds. Only about seventy-five simple substances were known, and none has ever been seen to turn into another, so one metal cannot become another. Because of this, the amount of each simple substance stays the same through every change, and chemistry follows where each one goes. A chemical formula, built from Latin letters each standing for a definite weight, shows both what a compound contains and how much. An element is not the simple substance itself but the unchanging stuff it shares with its compounds: charcoal, graphite and diamond are three bodies, one element, carbon.

Questions

1. Chalk splits into lime and a gas, yet neither lime nor the gas counts as a simple substance. Why not?
 - a. Because both are found only in nature, never in a laboratory.
 - b. Because both can themselves be split further: the gas into charcoal and oxygen, lime into calcium and oxygen.
 - c. Because both are heavier than the chalk they came from.
 - d. Because a gas can never be a simple substance.
2. Why must the amount of each simple substance stay the same through every chemical change?

- a. Because simple substances never take part in reactions at all.
 - b. Because chemists always weigh them very carefully.
 - c. Because a simple substance can be neither made nor broken down, and matter is never lost.
 - d. Because all simple substances weigh the same.
3. What does it mean to say that red mercury oxide contains oxygen?
- a. That it can give up mercury and oxygen and hand them to other bodies, not that oxygen gas is inside it.
 - b. That tiny bubbles of oxygen gas are trapped inside the red powder.
 - c. That the powder will slowly turn into oxygen if left in the air.
 - d. That the powder is a mixture of liquid mercury and oxygen gas.
4. Charcoal, graphite and diamond look and behave very differently. How does Mendeleev fit them together?
- a. They are three different elements that happen to be black or clear.
 - b. They are compounds of carbon with different amounts of oxygen.
 - c. Only diamond is a simple substance; the other two are mixtures.
 - d. They are three different simple substances of one and the same element, carbon.

Answers

1. **b)** A simple substance is one that cannot be split into others; the gas is charcoal joined with oxygen and lime is calcium joined with oxygen, so both are still compounds.
2. **c)** Joining the rule that nothing is made or lost with the fact that simple substances cannot be made or split, each one must come out of a change in exactly the amount it went in.
3. **a)** The composition of a compound describes the changes it can undergo; the oxide holds the element oxygen, not the gas itself, as steam holds the substance of ice but not ice.
4. **d)** A simple substance can come in several forms, while the element beneath them stays unchanged: charcoal, graphite and diamond are three bodies, one element.

Worked examples

What a formula tells about table salt Table salt is made of sodium and chlorine, one share of each, and the shares weigh 23 for sodium and 35.5 for chlorine. What part of every hundred grams of salt is sodium, and what part chlorine?

One share of sodium and one of chlorine together weigh 23 plus 35.5, that is 58.5.

Sodium's part of the whole is 23 out of 58.5, which is about 39.3 out of every hundred.

Chlorine's part is 35.5 out of 58.5, about 60.7 out of every hundred.

The two parts together make the whole hundred, as they must.

Answer: About 39.3 grams of sodium and 60.7 grams of chlorine in every 100 grams of salt.

Practice

1. An alchemist claims he can make gold from a mixture of iron and sulphur. Using the idea of simple substances, explain why he cannot.

Hint: Which simple substances are in what he starts with?

Answer: From given substances one can get only those containing the very same simple substances. Iron and sulphur contain no gold, and simple substances never turn into one another, so no gold can come out.

2. For a long time nobody had obtained fluorine on its own. Why was it still counted as an element?

Hint: Think about what chemists did know about fluorine.

Answer: Its compounds with other simple substances were known, and they were plainly unlike all other compounds. That showed there was an unchanging stuff in them, an element, even before the simple substance itself was obtained.

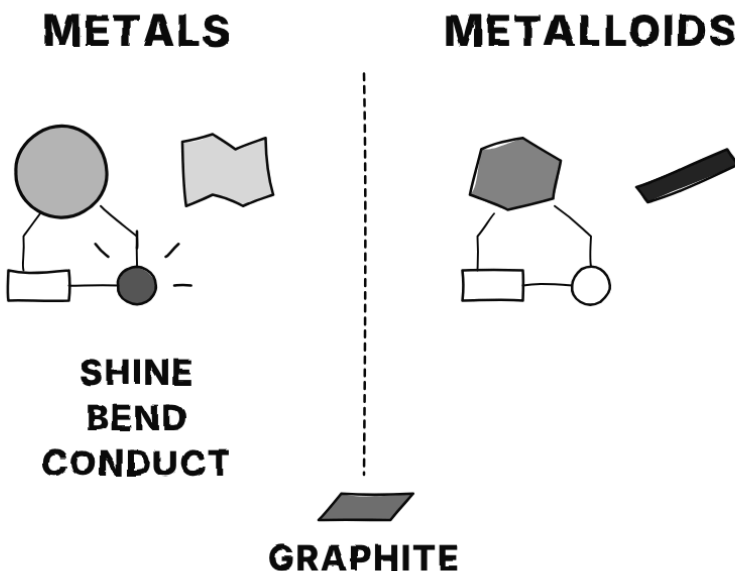
3. Explain in your own words the difference between a simple substance and an element, using steam and ice, or bread and grain.

Hint: Ask what is really present inside the compound.

Answer: A simple substance is a real body you can hold, like the metal mercury or oxygen gas. An element is the stuff of that body as it is present in compounds: red mercury oxide holds the elements mercury and oxygen, but not the liquid metal or the gas, just as steam holds the substance of ice but not ice, and bread the substance of grain but not grains.

A Roll Call of Simple Substances

Lay a handful of things on a table: a copper coin, a lump of sulphur, a stick of charcoal, a piece of aluminium foil. Tap each one, hold it up to the light, touch it to a battery's ends with a bulb in between. The coin and the foil shine, bend without breaking, feel cold, and carry the current; the sulphur and the charcoal do none of these things so well. That is the first rough sorting Mendelev offers among the simple substances.

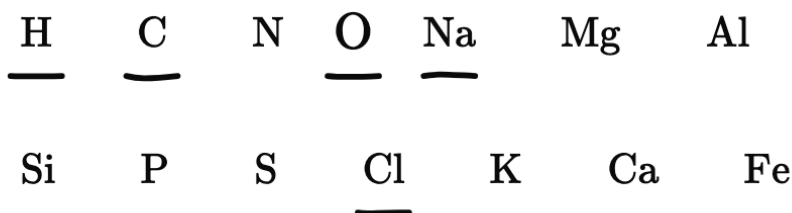


Metals and metalloids

Many simple substances, though not all, have a special lustre, let no light through, can be hammered thin, and conduct heat and electricity very well. Those are the metals, and their mixtures with one another, alloys, share the same features. The simple substances without these physical signs are called metalloids, a name that in Mendeleev's time meant non-metals. In sharp cases the two kinds are easy to tell apart, like copper and sulphur. But in many particular cases the difference is blurred, and so, Mendeleev warns, it cannot serve as an exact way to split the simple substances into two groups. Graphite from a pencil is a good example: it is not a metal at all, yet it has a grey shine and carries electricity well enough to be used in batteries.

Then Mendeleev calls the roll. About eighty simple substances were recognised in his day, though for about six of them the knowledge was still thin, because they are so rare and had been obtained in such tiny amounts. Only a small number of them make up the common bodies of nature, and these are the best studied, simply because so many people could work with them.

≈ 80 KNOWN



The fourteen commonest

The most widespread are about fourteen. Hydrogen is in water and in living things; carbon is in living things, coal and limestone; nitrogen is in the air and in living things. Oxygen is in air, water and the earth, and its total mass is the greatest of all. Then come sodium, in table salt; magnesium, in sea water; aluminium, in clay; silicon, in sand; phosphorus, in bones and plant ash; sulphur, in gypsum and sea water; chlorine, in salt; potassium, in saltpetre and plant ash; calcium, in limestone; and iron, in soil, ores and living things. A glass of tap water, a pinch of salt and a pencil already put five of them in your hands: hydrogen, oxygen, sodium, chlorine and carbon.

A second group is less common in nature but well used in daily life and industry. Here stand copper, zinc in brass and in galvanic cells,

nickel for plating other metals, silver, tin, platinum, gold, mercury and lead. Here too are lithium and iodine, used in medicine and photography, bromine, a brown volatile liquid, and arsenic, whose white compound is a poison. Others in this group colour things: cobalt gives blue glass, cadmium a yellow paint, and strontium the red of fireworks. The rechargeable battery in your phone runs on lithium, one of the substances on Mendeleev's list of things used in daily life.

IN DAILY USE

Cu Zn Ni Ag Sn Pt Au Hg Pb Li

RARER

Ti V W U Ga Ge Cs

INERT GASES

NO COMPOUNDS

He Ne Ar Kr Xe

RADIOACTIVE

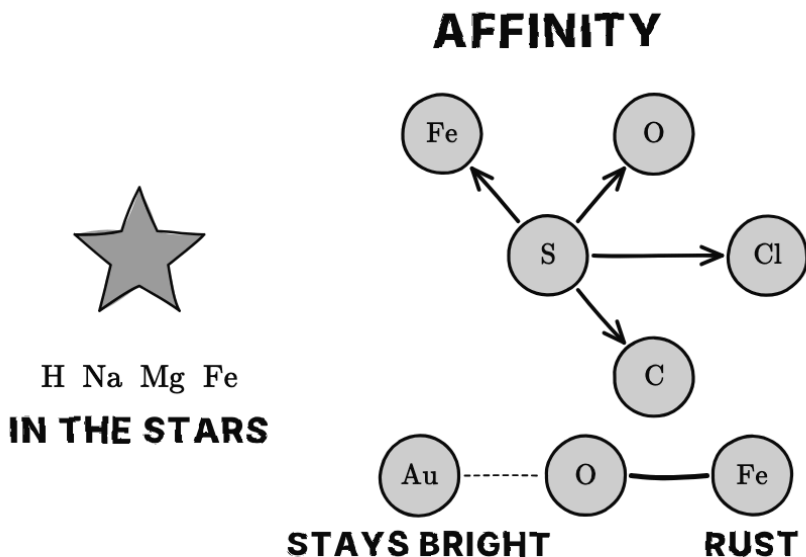
Ac Po Ra

Used, rare, inert, radioactive

A third group is well known and fairly often met, though in small amounts and with fewer uses: titanium, vanadium, tungsten, uranium and others. A fourth is rarer still, investigated in some detail but of no practical use yet: gallium, germanium, caesium, and a crowd of others. Then comes a striking group of gases discovered by Ramsay,

present in small amounts in the air: helium, neon, argon, krypton and xenon. They differ from all the rest in that nobody had managed to make them form a single compound with any other element. There was also some reason to count the metals actinium, polonium and radium, the last of them discovered by Madame Curie, found in the so-called radioactive substances mixed in small amounts with ores of uranium and thorium. Beyond these, a few more were listed, but they were so rare that it was not even settled whether some of them were truly separate. The neon sign above a shop and the argon inside many light bulbs both use these gases precisely because they hardly react with anything.

Are the simple substances found only on Earth? No: by studying the light of distant stars, scientists had proved that many of the commonest simple substances, such as hydrogen, sodium, magnesium and iron, are present there too. So the same building blocks reach far across the universe. Why some of them are so much more plentiful than others, Mendeleev says, nobody yet knew.



Same bricks, different appetites

What marks each element is its readiness to combine with others, making compounds that are more or less stable and may join into still more complex ones. Sulphur combines easily with metals, with oxygen, with chlorine and with carbon. Silver and gold combine reluctantly, and many of their compounds are weak and fall apart when heated. The cause that drives substances into chemical change, and that afterwards holds the different elements together in their compound, is called affinity, or chemical affinity. Gold jewellery stays bright for centuries while an iron gate rusts in a single winter: that is the difference in affinity, felt in everyday life.

What kind of force is affinity? It only pulls, like gravity, and so some scientists, Bergman and Berthollet among them, thought it might be

gravity itself, only acting at the tiniest distances. But gravity depends only on the masses and the distance, while affinity depends strongly on what the substances are. Nor is it the same as cohesion, the force that holds a single substance together, gives a crystal its shape and makes a liquid form drops, because affinity acts between different substances. Nor is it the stickiness that makes two polished plates cling, or water wet glass: when things stick, each stays itself, but in a chemical change one substance enters the other and something new is formed. Those clinging forces, acting only on full contact, are a kind of bridge between mechanical and chemical forces.

For a long time, especially in the first half of the nineteenth century, chemical forces were thought to be electrical. There is a close tie: chemical changes produce electricity, and an electric current can split compounds. But heat is tied to chemistry just as closely, since reactions give off heat and heat can split substances. That only shows the unity of the forces of nature, how one can give rise to another; and the electrical theory did not stand up to testing.

The nature of chemical force is still as hidden, Mendeleev says, as the nature of gravity. Yet astronomy learned to predict the heavens in detail without knowing what gravity is, and in the same way there is hope for chemistry through the theory of heat, the best understood of all the molecular phenomena. This young field, which Mendeleev prefers to call chemical mechanics, is still being worked out. It assumes you already know the substances, their changes and what accompanies them, and so it can come only after the basic ideas and substances of chemistry, which are the main aim of his book.

Remember

Metals shine, bend and carry heat and electricity, and metalloids lack these signs, but the line between them is blurred and cannot sort the simple substances exactly. About eighty simple substances were known, and a small number of them, with oxygen the most plentiful, make up most of nature, while others serve industry and medicine. The same simple substances are found in distant stars, so they reach far across the universe. Each element is marked by its readiness to combine, and the force behind this, chemical affinity, is not gravity, cohesion, stickiness or electricity. Its nature is still hidden, and its study, chemical mechanics, has to come after the substances themselves are known.

Questions

1. Why does Mendeleev say the split into metals and metalloids cannot sort the simple substances exactly?
 - a. Because metals and metalloids weigh the same.
 - b. Because only a few simple substances were known.
 - c. Because in many particular cases the difference in shine, malleability and conduction is blurred.
 - d. Because metalloids can be turned into metals by heating.
2. What did the study of light from distant stars show about simple substances?

- a. That common simple substances such as hydrogen, sodium and iron are present there too.
 - b. That the stars are made of entirely different simple substances.
 - c. That simple substances turn into one another inside stars.
 - d. That only gases exist in the stars.
3. Why can chemical affinity not simply be gravity acting at small distances?
- a. Because affinity pushes substances apart, while gravity pulls.
 - b. Because gravity works only on Earth.
 - c. Because affinity works only in sunlight.
 - d. Because gravity depends only on mass and distance, while affinity depends strongly on which substances meet.
4. What separates a chemical change from two polished plates sticking together?
- a. Sticking needs heat, chemical change does not.
 - b. In a chemical change one substance enters the other and something new forms; in sticking, each stays itself.
 - c. Sticking happens only between metals.
 - d. There is no difference: both are affinity.

Answers

- 1. c)** In sharp cases like copper and sulphur the two kinds are easy to tell apart, but in many cases the signs are blurred, so the split is only rough.
- 2. a)** The light of distant stars showed the commonest earthly simple substances there as well, so the same building blocks reach far across the universe.

3. d) Gravity does not care what a body is made of; affinity does: sulphur combines eagerly, gold reluctantly.

4. b) When things cling, each remains what it was; in a chemical change one substance penetrates the other and a new substance is formed.

Practice

1. A friend says chemical forces must be electrical, since batteries make electricity from chemicals and a current can split compounds. How would Mendeleev answer?

Hint: Think about how heat is linked to chemical change too.

Answer: The tie is real, but heat is linked just as closely: reactions give off heat, and heat can split substances. These ties show the unity of the forces of nature, how one gives rise to another, not that chemical force is electricity; the electrical theory failed when tested.

2. Gold rings stay bright for centuries, while iron rusts quickly. Explain this with the idea of affinity.

Hint: Compare how readily each metal combines with other elements.

Answer: Each element is marked by its readiness to combine. Iron combines readily with oxygen from the air and rusts, while gold combines reluctantly and its compounds are weak, so gold stays as it is.

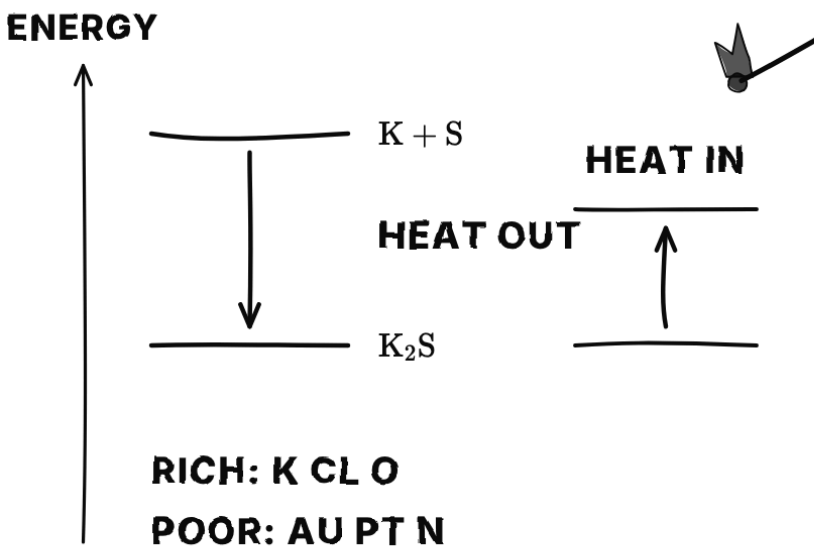
3. Why does Mendeleev put chemical mechanics after the study of substances, and not at the start?

Hint: What does chemical mechanics take for granted?

Answer: Chemical mechanics studies the forces and energy behind chemical change, and it assumes you already know the substances, the changes they undergo and what accompanies them. So it can only come after the basic ideas and substances of chemistry.

Energy Stored in Substances

Strike a match. For a moment nothing seems to happen, then a flame leaps up and gives off heat and light that were nowhere to be seen a second before. Where were they hiding? Mendeleev's answer is that substances carry a hidden store of energy, and that every chemical change spends some of it or tops it up.



The hidden store of energy

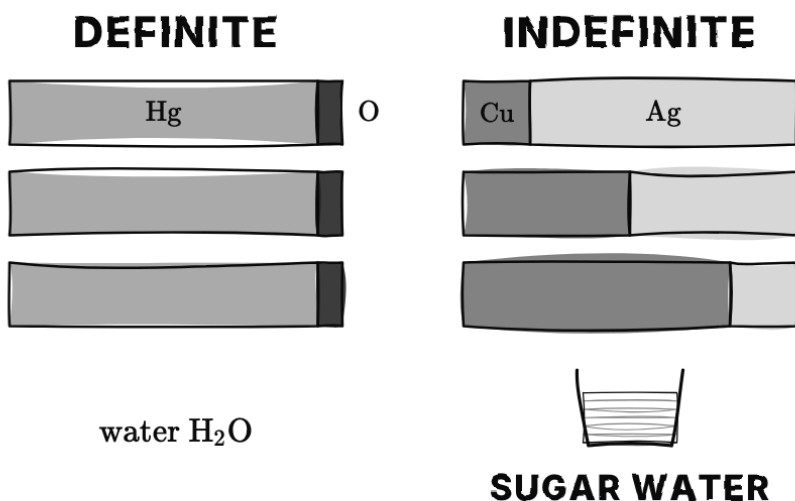
His reasoning runs like this. Chemical changes come from forces inside the substances, and they always involve the movement of tiny particles. Physics had shown that energy is never lost, only changed

from one form to another. So substances, and the elements in particular, must hold a store of chemical energy, a kind of invisible motion that urges them to react. When a reaction gives off heat, part of that chemical energy has turned into heat. When a reaction takes in heat, part of that heat has been hidden away as chemical energy. A phone battery is exactly such a store: charging it pushes energy into its chemicals, and using the phone lets the chemicals spend it again.

After several combinations that each give off heat, a compound may have spent most of its store and become sluggish, unwilling to react. Yet even such a tired compound can sometimes join with an energetic substance and form a new, still more complex body that is ready to react again. Among the simple substances, gold, platinum and nitrogen have little energy, while potassium, chlorine and oxygen have a great deal. When two very unlike substances combine, the product often has less energy than either. Potassium and sulphur, once heated, both burn readily in air. But the compound of the two, though it can still take up oxygen, does not burn in air as its parts do, because much of their energy left as heat when they joined. Just as heat is taken in or given out when ice melts or water freezes, so every chemical change alters the store of chemical energy, and heat goes in or out with it.

What, then, does one need to know to understand chemistry as a kind of mechanics, to follow how reactions run? Mendeleev names five things. First, stoichiometry, the part of chemistry that studies the proportions, by weight and by volume, in which substances react. Second, the different kinds and classes of chemical interaction. Third, how properties change when composition changes. Fourth, the phenomena that accompany chemical change. And fifth, the conditions under which reactions happen.

Of these, stoichiometry is by far the best worked out. Its laws, found by Dalton, by Avogadro and Gerhardt and others, run so deep through every part of chemistry that Mendeleev calls his whole era the age of applying them to particular cases. So the rest of his book follows the laws of proportion. They even gave birth to a new way of sorting compounds into definite and indefinite ones.



Fixed and free proportions

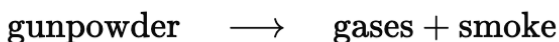
At the start of the nineteenth century Berthollet still made no such distinction. Then Proust showed that very many compounds contain their parts in a perfectly fixed proportion by weight, which never changes under any conditions. Red mercury oxide is an example: it always holds mercury and oxygen in the same fixed proportion, which its formula expresses. In an alloy of copper and silver, on the other

hand, you can add as much of either metal as you like, just as you can make sugar water as sweet or as weak as you please, and still get a uniform whole. Those are indefinite compounds. Alloys and solutions matter just as much in nature, in laboratories and in factories, but since the laws of proportion had been applied mostly to definite compounds, knowledge of the indefinite ones was still thin. Coffee with sugar is an indefinite mixture you adjust to taste; the water in it, always the same two elements in the same proportion, is a definite compound.

For chemical mechanics it is also vital to tell reversible reactions from irreversible ones. Salt dissolves in water at room temperature, and at that same temperature the solution can give the salt back as the water evaporates. Iron, at a certain heat, takes oxygen from water and sets hydrogen free; yet at that same heat hydrogen can take the oxygen back and give iron and water again. When a reaction can run both ways, starting from either side you end up with all the substances together, in a balance, a chemical equilibrium. Add more of one substance, and the balance shifts, so reversible reactions let chemists study how the amount of a substance steers a change.



EQUILIBRIUM

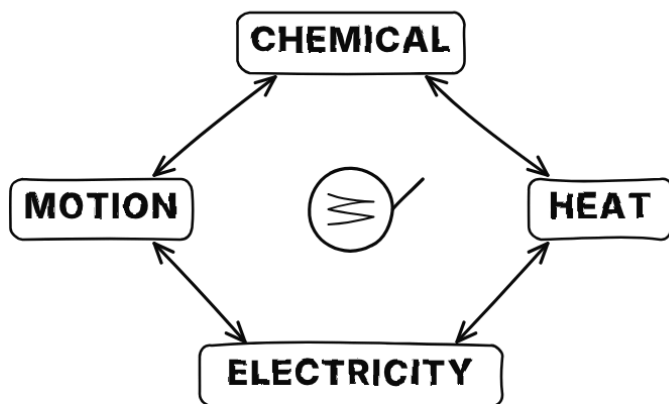
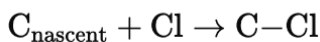
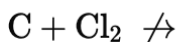


Both ways, or one way

Other reactions run only one way. Many complex substances of plants and animals fall apart in heat, and their pieces never rejoin at any temperature. Gunpowder, a mixture of saltpetre, sulphur and charcoal, burns to gases and smoke that never turn back into powder. A baked cake is irreversible in just this sense: no oven setting will turn it back into flour, eggs and sugar.

Even when two substances will not combine directly, there may be a roundabout way. Chlorine does not react with charcoal, graphite or diamond, yet many firm compounds of chlorine and carbon exist. They are made by letting chlorine act on compounds of carbon and hydrogen: the chlorine pulls away the hydrogen, and the carbon, freed at that very moment, joins with some of the chlorine. Chemists

explain this by saying that a substance at the moment of its release, in the nascent state, is especially ready to combine.



NO THEORY YET

Forces turn into one another

Finally, chemical changes produce motion, heat, light, electrical tension and current, and all these, in their turn, can change chemical reactions. This two-way traffic is natural, Mendeleev says, because all the phenomena of nature are only different kinds of motion, visible or invisible. Sound and then light turned out to be vibrations. The link between heat and mechanical work became certain, and a fixed amount of work was found to match each unit of heat. And a dynamo, such as Gramme's machine, gives a current when you turn it, while sending a current through it makes it turn. An electric bicycle shows the same two-way link: its motor drives the wheels from the battery,

and on some models braking turns the motor into a dynamo that charges the battery again.

So chemical mechanics must build on these ties between chemistry, physics and mechanics. But Mendeleev is frank: because the subject is so complex and so new, it has no orderly theory yet, not even a satisfactory hypothesis. He therefore leaves it to physical chemistry as a separate branch of science, and does not dwell on it in his book.

Remember

Substances hold a store of chemical energy, a hidden motion that urges them to react, and every reaction changes that store, giving out or taking in heat. Some simple substances, like potassium, chlorine and oxygen, are rich in energy, and others, like gold, platinum and nitrogen, poor, while compounds of unlike substances are often less energetic than their parts. The laws of proportion, the best developed part of chemistry, separate definite compounds of fixed composition from indefinite ones like alloys and solutions. Some reactions can run both ways and reach a balance, others only one way, and substances that will not join directly may still join in the nascent state. Chemical, thermal, electrical and mechanical phenomena turn into one another, yet chemical mechanics still has no satisfactory theory.

Questions

1. Potassium and sulphur both burn readily in air, but their compound does not. Why?
 - a. Because the compound contains no potassium or sulphur any more.
 - b. Because much of their chemical energy left as heat when they combined.
 - c. Because the compound is too heavy to burn.
 - d. Because air cannot reach the inside of the compound.
2. What makes red mercury oxide a definite compound, and an alloy of copper and silver an indefinite one?
 - a. The oxide always holds its parts in the same fixed proportion, while the alloy can be made in any proportion.
 - b. The oxide is red and the alloy is silvery.
 - c. The oxide can be decomposed, while the alloy cannot be separated at all.
 - d. The oxide is found in nature, the alloy only in factories.
3. What happens in a reversible reaction if you start from either side?
 - a. The reaction stops as soon as it starts.
 - b. Only the products appear, never the starting substances.
 - c. All the substances end up present together in a balance.
 - d. The substances turn into an indefinite compound.
4. Chlorine does not react with charcoal, graphite or diamond. How can compounds of chlorine and carbon still be made?
 - a. By heating chlorine with diamond until it melts.
 - b. By passing an electric current through charcoal.

- c. By mixing chlorine with burned gunpowder.
- d. By letting chlorine act on compounds of carbon and hydrogen, so the freed carbon joins chlorine in the nascent state.

Answers

- 1. **b)** When unlike substances combine, part of their store of energy is given off as heat, so the product has less energy than its parts.
- 2. **a)** Proust showed that many compounds have a fixed proportion by weight that never changes, while in an alloy or solution you can vary the amounts freely.
- 3. **c)** Since the reaction can run both ways, starting from either pair you end with all the substances together, a chemical equilibrium.
- 4. **d)** Chlorine takes away the hydrogen, and the carbon, freed at that moment, is especially ready to combine and joins with part of the chlorine.

Practice

- 1. A reaction gives off a lot of heat. What has happened to the chemical energy of the substances, in Mendeleev's terms?

Hint: Energy is neither lost nor created, only changed in form.

Answer: Part of the substances' store of chemical energy has turned into heat. The products therefore hold less chemical energy than the starting substances did, and to reverse the change that energy would have to be put back in.

- 2. Give one example of a reversible and one of an irreversible change from the lecture, and explain the difference.

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

Answer: Salt dissolving in water is reversible: at the same temperature, evaporation gives back the salt and the water. Burning gunpowder is irreversible: its gases and smoke never turn back into saltpetre, sulphur and charcoal at any temperature.

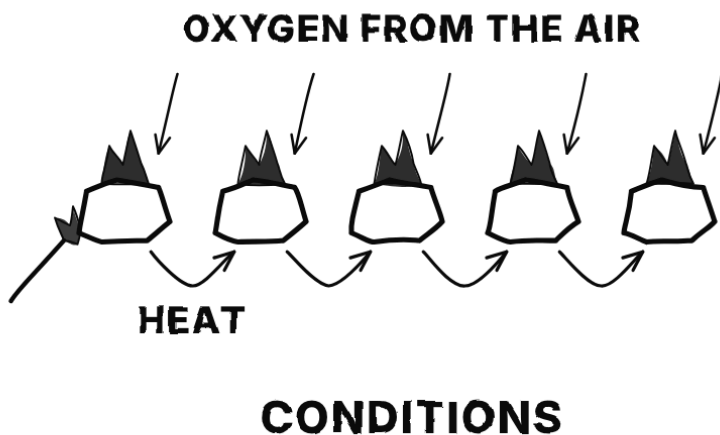
3. Why does Mendeleev not build his book on chemical mechanics, even though he thinks it is important?

Hint: What does he say about the state of its theory?

Answer: Because the subject is very complex and new, it has no orderly theory and not even a satisfactory hypothesis yet. So he leaves it to physical chemistry as a separate branch and builds his book on the laws of proportion, which are well established.

Heat and Current Decide

A lump of charcoal can sit in the open air for years and never burn. Yet the oxygen it needs is touching it the whole time. Hold a match to one corner until it glows, and the fire spreads by itself until nothing is left but ash. So having the right substances is not enough: something else must also be right. Mendeleev calls this something the conditions of a reaction.

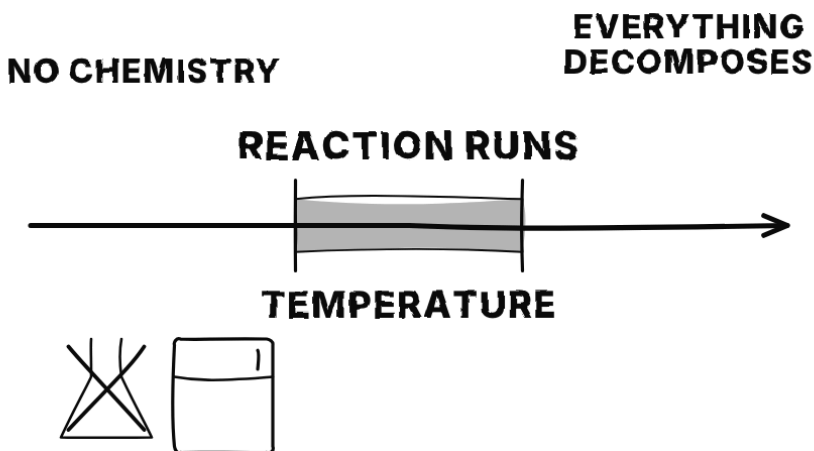


Heat passes the fire along

He explains the charcoal like this. The glowing part combines with the oxygen of the air, and that combining gives off heat. The heat makes

the next part glow, and that part burns only because it was heated first. Each reaction, in the same way, goes only under certain physical, mechanical and other conditions, often quite unlike the everyday conditions in which substances lie around us. A barbecue shows it every summer: the coals sit cold in the bag, and only the lighter's flame sets the chain going.

The first and most important condition is temperature. Combinations happen only within certain limits of temperature, and outside them they do not happen at all. Burning starts only when the fuel is hot; and, surprisingly, some compounds of chlorine or of table salt with water form only below freezing, and break up again when warmed.

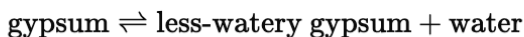
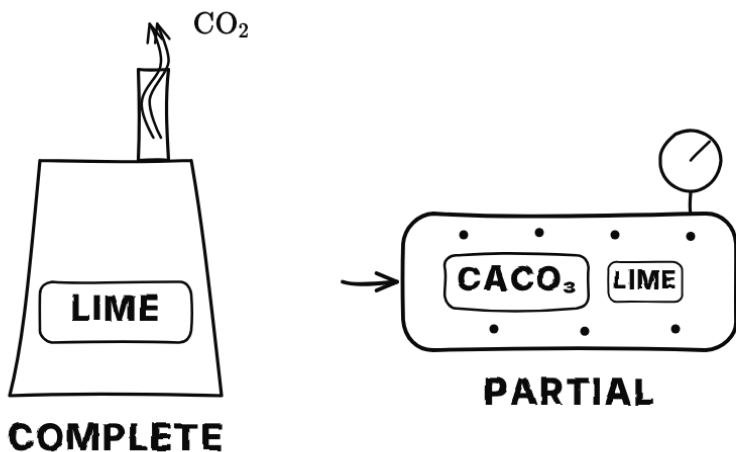


Every reaction has its window

Why should heat help a reaction? Mendeleev gives two reasons. Heat may turn a solid into a liquid or a vapour, and a liquid lets the particles touch fully, which a reaction needs. And heat loosens cohesion, the inner bond between the particles of one substance, so they come apart more easily and can form new compounds. When a reaction actually needs heat, as a decomposition does, the need is plain. Indeed, all compounds fall apart if the heat is strong enough, like the red mercury oxide and the wood we met earlier. Some go at a fairly mild heat: the fulminate in a gun's percussion cap decomposes just a little above the boiling point of water, and much of the tissue of plants and animals breaks down in an ordinary oven.

Cold works the other way. At very low temperatures no chemical change happens at all; plants stop their chemistry in the winter frost. Raoul Pictet, using the extreme cold of boiling liquefied gases, found that even violent reactions, such as an acid with caustic soda or with sodium metal, do not happen when it is cold enough, and that litmus does not even change colour. So every reaction has its own range of temperature, and on the scorching sun or the frozen moon many of the changes we see on Earth surely cannot take place. Your freezer works on this very idea: food keeps for months because the chemistry of spoiling slows almost to a stop in the cold.

Heat has a special lesson for reversible reactions. Warm a compound that can re-form from its own products, and when decomposition begins, it does not run to the end at once. Only a part breaks down while the rest stays whole; raise the temperature, and a larger part breaks down; at each temperature there is a fixed share of broken to unbroken, until finally it all comes apart. This partial decomposition by heat is called dissociation, an idea brought into science by Henri Sainte-Claire Deville.

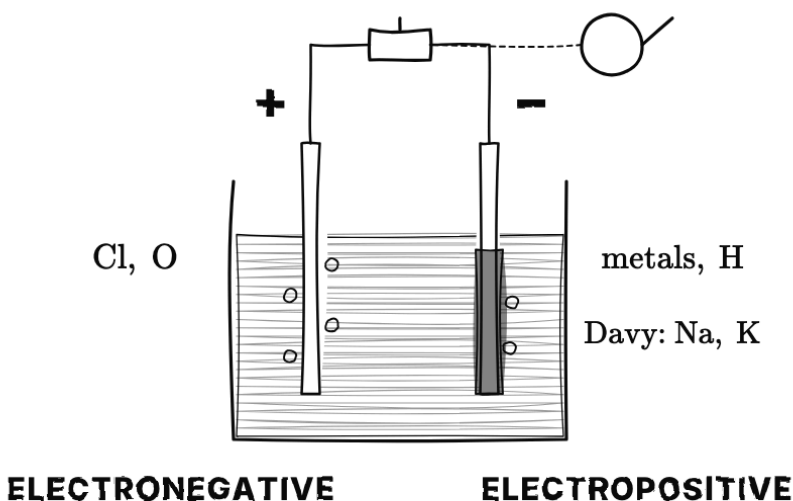


Open kiln, sealed barrel

Limestone shows how it works. In a lime kiln, the stone breaks down completely into lime and carbon dioxide, because the gas can escape up the chimney. But seal the same stone tightly inside a gun barrel and heat it, and only part of it breaks down, because the gas cannot get away. The breakdown stops when the trapped gas reaches the highest pressure that belongs to that temperature. Pump in more gas, and lime and gas begin to combine again; let some out, and decomposition resumes. It is just like water evaporating in a closed jar, which stops when the vapour is as dense as that temperature allows, and starts again if some vapour is let out. A screw-top jar half full of water is the kitchen version: with the lid on, the level stops falling once the air above holds all the vapour it can; take the lid off and the water slowly goes on evaporating.

Sometimes a change even has an exact temperature, like a melting or boiling point. Natural gypsum, sealed so that its water cannot escape, falls apart above a certain temperature into a wet paste: most of its water comes out as liquid, and a gypsum with far less water remains. Cool it below that temperature, and the original gypsum forms again. The switch is so sharp that it can be spotted by a sudden change in volume. Plaster of Paris for casts is made by heating gypsum, and it sets hard again when mixed with water.

The second great condition is electricity, and its influence is much like that of heat. Most compounds that conduct an electric current are split by it, and, just as with heat, combination often happens close to the conditions of decomposition. Electricity, Mendeleev says, should be seen as another kind of motion of tiny particles, like heat. Its great advantage is that it can split even the most stable compounds at ordinary temperature.



Current sorts the parts

And it does something heat never does: the parts appear at different places, at the two poles, or electrodes, where the current enters and leaves. Substances that gather at the positive pole, mostly non-metals such as chlorine and oxygen, and acids, are called electronegative. Metals and hydrogen gather at the negative pole and are called electropositive. Recharging a car battery is this sorting at work: the current drives each part of the chemicals back to its own electrode.

Splitting compounds by current led to some of the greatest discoveries in chemistry. Lavoisier and his contemporaries could not decompose the compounds of potassium and sodium with oxygen. The Englishman Davy did it with a galvanic current, and collected the metals potassium and sodium themselves at the negative pole. In

Mendeleev's own time, dynamos driven by fuel or by water power made current cheap, and Davy's method entered the factory: sodium from molten caustic soda, and chlorine from solutions of table salt.

Remember

A reaction depends not only on the substances but on the conditions around them; charcoal needs to be heated before it will burn. Each reaction has its own range of temperature: heat helps by bringing particles into contact and loosening cohesion, strong heat decomposes every compound, and great cold stops chemistry altogether. In reversible reactions, heat causes dissociation, a partial decomposition that settles at a fixed share for each temperature and depends on whether the products can escape. Electric current acts much like heat, splitting compounds even at room temperature, with non-metals going to the positive pole and metals and hydrogen to the negative one. With current, Davy first obtained potassium and sodium, and dynamos later made the method a factory process.

Questions

1. Charcoal lies in air for years without burning, yet burns completely once one corner is lit. Why does the fire keep going?
 - a. The burning part gives off heat that makes the next part hot enough to burn.

- b. The match adds a special substance that spreads through the charcoal.
 - c. The air becomes richer in oxygen once a fire starts.
 - d. The charcoal turns into a liquid that burns more easily.
2. Limestone breaks down completely in a lime kiln, but only partly when sealed in a heated gun barrel. Why?
- a. The gun barrel is never as hot as a kiln.
 - b. Iron from the barrel combines with the lime.
 - c. In the kiln the carbon dioxide escapes, while in the sealed barrel it builds up until decomposition stops.
 - d. Limestone in a sealed space turns into gypsum instead.
3. Why do many reactions we see on Earth surely not happen on the moon?
- a. Because the moon has no oxygen-free gases.
 - b. Because there is no electricity on the moon.
 - c. Because substances on the moon are different elements.
 - d. Because each reaction needs its own range of temperature, and the moon is far too cold.
4. When an electric current splits a compound, what happens that heating never does?
- a. The compound gets heavier.
 - b. The parts appear at different poles: non-metals at the positive one, metals and hydrogen at the negative one.
 - c. The compound turns into a simple substance without any products.
 - d. All the parts collect together at the positive pole.

Answers

- 1. a)** Combining with oxygen gives off heat, and that heat makes the next part glow; each part burns only because it was heated first.
- 2. c)** Dissociation goes to the end only if a product can get away; trapped gas reaches the highest pressure for that temperature and the breakdown stops.
- 3. d)** At very low temperatures chemical change stops, as Pictet showed, so the moon's cold rules out many earthly reactions.
- 4. b)** With current, the parts separate at the two electrodes: electronegative substances at the positive pole, electropositive ones such as metals at the negative.

Practice

- 1.** Lime and carbon dioxide are sealed in a heated vessel where some limestone has dissociated. What happens if you pump in more carbon dioxide, and what if you let some out?

Hint: Compare with vapour over water in a closed jar.

Answer: Pumping in more gas makes lime and gas combine back into limestone; letting gas out makes more limestone decompose. Just as with evaporation, each temperature has a highest pressure, and the change runs toward it.

- 2.** Give Mendeleev's two reasons why heating helps substances combine.

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

Answer: Heat can turn a solid into a liquid or vapour, which lets the particles touch fully, as a reaction needs. And heat weakens cohesion, the

inner bond between particles of one substance, so they separate more easily and can form new compounds.

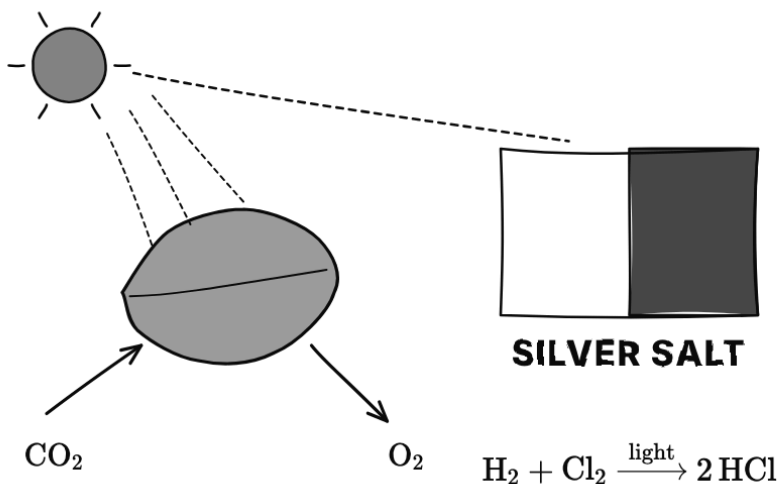
3. Why could Lavoisier not obtain potassium and sodium, while Davy could?

Hint: What could the electric current do that heat could not?

Answer: The compounds of potassium and sodium with oxygen are too stable to be split by the methods of Lavoisier's day. Davy used a galvanic current, which can split even the most stable compounds, and collected the metals at the negative pole.

Light, a Blow, Time and Touch

Leave a houseplant on a sunny windowsill and it quietly does something no laboratory of Mendeleev's time could copy. It takes carbon dioxide, a gas that neither heat nor current easily breaks, splits it in the light, and gives off oxygen. Heat and electricity are not the only conditions that steer chemistry; Mendeleev ends his introduction with four more.



Light splits and joins

The first is light. Light can break down certain unstable compounds, and photography rests on this property of some silver salts. The

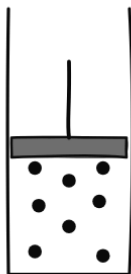
vibrations that make up light carry very little mechanical work, so under ordinary conditions only fragile compounds are split by it. But in plants, light drives a host of decompositions and combinations, many not yet copied by any artificial means, and this remained an unsolved problem of chemistry. Light can also make substances combine: chlorine joins with hydrogen not only when heated but also when lit. A pair of glasses that darken in bright sun owes its trick to the same kind of light-sensitive silver compound as an old photograph.

The second is mechanical action. Some substances fall apart from mere friction or a blow, such as nitrogen iodide, and the fulminate in a gun's percussion cap, set off by the hammer's strike. Rubbing makes sulphur burn with the oxygen contained in Berthollet's salt. Pressure matters too, above all for gases: squeezing a gas crowds its particles together, so different substances meet far more often, and compressed hydrogen acts more strongly on iodine and on many salt solutions. Striking a safety match is mechanical action at work: the rub of the head on the box starts a reaction that then feeds itself.

BLOW



PRESSURE



TIME

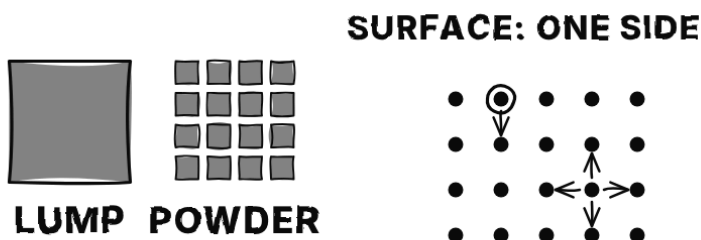


A blow, pressure, time

The third is time. Substances must first move into contact, as when a solid burns only at its surface and fresh air must keep flowing to it. And even after full contact, the change inside needs time and runs at a definite speed. Mendeleev's example is wine. Young wine holds acids and alcohol separately; as it ages, they slowly react and give water and fragrant esters, the wine's bouquet. This reaction is slow at ordinary temperature, and reversible, and its speed depends on temperature and other conditions. Most of the sharp reactions a beginner meets, though, go so fast that time is usually left out of account.

The fourth is the state of contact. The more points of contact, the more vigorous the reaction. Sulphuric acid hardly takes up a certain oily gas when they simply touch, but with long shaking it does,

because the points of contact grow enormously. Solids must be ground as fine as possible and mixed well if they are to react fully and fast. The Belgian chemist Spring showed that powders of solids which do not react at room temperature will do so under enormous pressure: sulphur then joins many metals, and metal powders form alloys. So even solids can react, because in every state of matter the particles keep some inner motion.



PT SPONGE

More contact, faster change

Mendeleev adds a subtle point. A particle inside a substance is pulled by its neighbours from all sides, but a particle at the surface only from one side. So at a surface the state of matter is altered, rather as if it had been heated. This explains a large class of contact reactions, set going by the mere presence of certain substances, especially porous or

powdery ones like spongy platinum and charcoal. Sulphur dioxide will not combine with oxygen directly, yet in the presence of spongy platinum it does, giving off heat. The catalytic converter in a car's exhaust works on this very principle, using a thin coat of platinum metals to make harmful gases react.

These general ideas, Mendeleev says, gain their real meaning only through the particular substances, which the book now turns to. Still, the great laws of the conservation of matter and of energy had to come first, because only with them in hand can the details be studied fruitfully.

Remember

Light splits fragile compounds, as in photography, can make chlorine and hydrogen combine, and in plants breaks even carbon dioxide, giving off oxygen. Blows, friction and pressure can start reactions, and pressure brings gas particles together more often. Reactions take time, like the slow ripening of wine's bouquet, though the sharpest ones are so fast that time is usually ignored. More points of contact mean faster reactions, and surfaces of substances such as spongy platinum can set reactions going by their mere presence. All these details rest on the two great laws laid down at the start: matter and energy are never created and never lost.

Questions

1. Why can light split only certain fragile compounds under ordinary conditions?
 - a. Because the vibrations of light carry very little mechanical work.
 - b. Because light cannot pass through most substances.
 - c. Because light only acts at very low temperatures.
 - d. Because only silver can absorb light.
2. Why does long shaking help sulphuric acid take up a gas it barely touches when left still?
 - a. Shaking heats the acid to its boiling point.
 - b. Shaking turns the gas into a liquid.
 - c. Shaking greatly increases the number of points of contact.
 - d. Shaking removes the oxygen from the gas.
3. Why does wine develop its bouquet only after long storage?
 - a. Because the alcohol slowly evaporates.
 - b. Because light slowly enters the bottle.
 - c. Because the grapes keep growing inside the wine.
 - d. Because its acids and alcohol react slowly at ordinary temperature to give fragrant esters.
4. How does spongy platinum make sulphur dioxide combine with oxygen?
 - a. The platinum itself combines with the oxygen and is used up.
 - b. At its surface the state of matter is altered, rather as if heated, which sets the reaction going.
 - c. It gives off an electric current.
 - d. It absorbs the light needed for the reaction.

Answers

1. **a)** The vibrations that make up light carry little work, so they can break only unstable compounds such as the silver salts of photography.
2. **c)** The more points of contact, the more vigorous the reaction, and shaking multiplies them enormously.
3. **d)** The reaction between acids and alcohol runs at a limited speed at ordinary temperature, so the fragrant esters appear only with time.
4. **b)** Particles at a surface are pulled from one side only, so their state is changed as if heated; porous bodies like spongy platinum start contact reactions this way.

Practice

1. Name four conditions other than heat and electricity that Mendeleev says can steer chemical change, with one example of each.

Hint: Think of light, a blow, the clock and contact.

Answer: Light, which splits silver salts in photography and makes chlorine join hydrogen; mechanical action, such as the blow that sets off fulminate in a percussion cap; time, as in the slow formation of wine's bouquet; and the state of contact, as when shaking or fine grinding speeds a reaction.

2. Spring made powders of sulphur and metals react at room temperature. How, and what does that show about solids?

Hint: What did he apply to the powders?

Answer: He pressed them under enormous pressure, which greatly increased the surfaces of contact. It shows that solids, too, can react, because particles keep some inner motion in every state of matter.

3. Why does Mendeleev introduce the laws of conservation of matter and energy before the details of particular substances?

Hint: What role do they play in studying the details?

Answer: Because only with these broad laws accepted can the study of particular substances be manageable and fruitful; the general ideas get their full meaning from the details, but the details need the laws as their framework.