

The Principles of Chemistry



Dmitri Mendeleev · 1903

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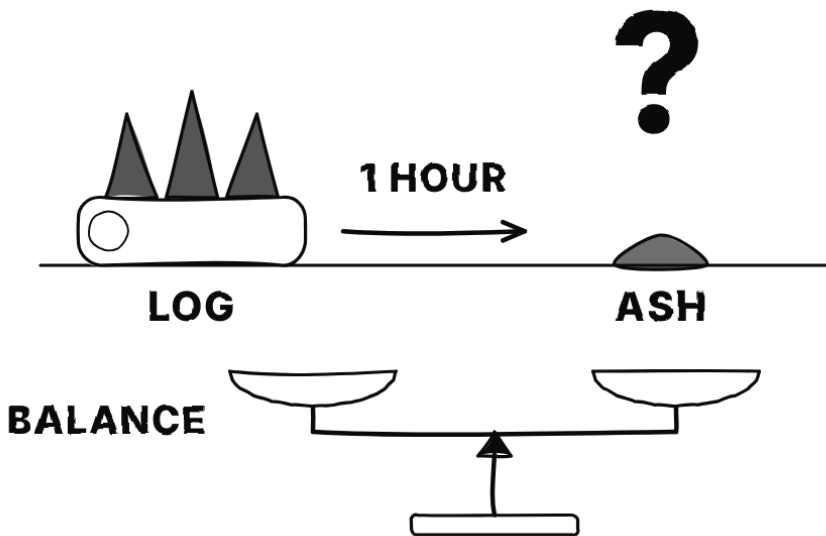
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Where Does the Wood Go?

Picture a log in a fireplace on a winter evening. An hour later there is only a small heap of grey ash that you could hold in one hand. Where did the rest of the wood go? For thousands of years the honest answer seemed to be that it simply vanished, and that fire destroys matter. The book you are reading opens by showing that this answer is wrong, and that the way to prove it is a balance.

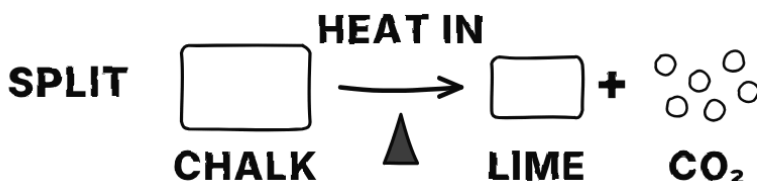
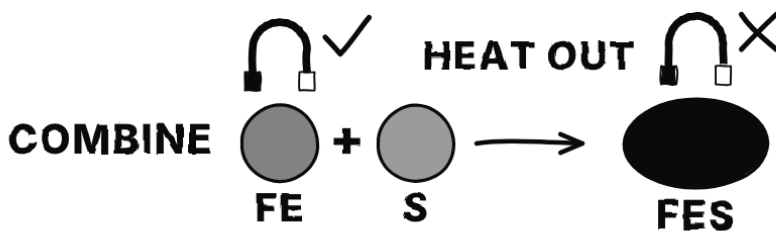


Where Does the Wood Go?

Mendeleev begins with a definition. Chemistry, he says, studies the homogeneous substances of which all the bodies of the world are

made, how they turn into one another, and what happens while they do. A homogeneous substance is one that is the same all through, like pure water, pure iron or pure sugar. He adds that chemistry became a science of its own because people had to admit a new kind of force. Besides gravity, cohesion, heat, light and electricity, there are inner forces in the tiniest parts of every substance. These forces are hidden in ordinary life, and they show themselves only when one substance changes into another. Such a change is called a chemical reaction. A reaction happens only when the substances touch each other as closely as possible, and it is governed by the forces of their smallest invisible particles, which Mendeleev calls molecules.

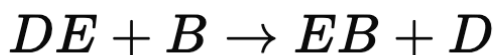
He then sorts reactions into three main kinds. The first is combination: two substances, or in general several, give a smaller number of substances, most simply just one. His example is iron and sulphur. Mix iron filings with yellow sulphur powder and you have a mere mixture: a magnet pulls the iron out, and an oily liquid can wash the sulphur away. Heat the mixture, and a new substance appears, iron sulphide, in which no microscope can find a grain of iron or a grain of sulphur. The two have entered each other completely and can no longer be told apart or picked apart. Combination usually gives out heat. Ordinary burning is this kind of reaction: the fuel combines with one part of the air, the part called oxygen, and the gases and vapours of flame and smoke are what it forms. The gas flame on your kitchen stove is a combination happening in front of you, fuel joining oxygen and giving out the heat that boils the kettle.



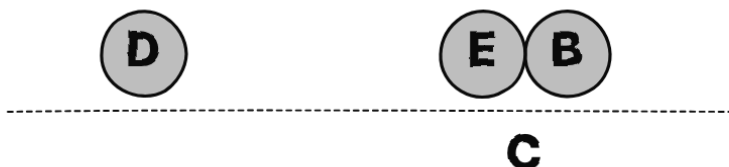
Combination and Decomposition

The second kind is decomposition, the opposite case. Here one substance gives two or more. Heat wood strongly without air, and it falls apart into a gas that burns, a watery liquid, tar, and charcoal; factories once made tar, lighting gas and charcoal exactly this way. Heat limestone, chalk or marble, and they leave lime behind while a gas escapes, which Mendeleev calls carbonic acid gas and we call carbon dioxide. The green copper compound in the mineral malachite does the same thing at a much lower heat, low enough that a thin glass tube survives it; he promises to describe this case closely in a moment. And while combination usually gives out heat, decomposition usually takes heat in.

The third kind is the one that needs a formula, and it is worth slowing down for it. Here the number of substances going in equals the number coming out: two give two. Mendeleev writes it with letters. Take two bodies, A and B, and suppose they produce two others, C and D. Imagine that A is really made of two parts, D and E, so that A can be written $A = DE$. Now let A split into D and E, and let E join B to make C, so that $C = EB$. Written in one line, the reaction is $DE + B \rightarrow EB + D$. In words: the part E has moved from one partner to another, and D has been left on its own. The intuition is a dance where one dancer changes partners: nobody new enters the hall, and nobody leaves it, but the pairs are different at the end. So this third kind is a decomposition and a combination happening together, and Mendeleev calls such reactions displacements, or, when two substances give two new ones, substitution or double decomposition.



2 IN → 2 OUT

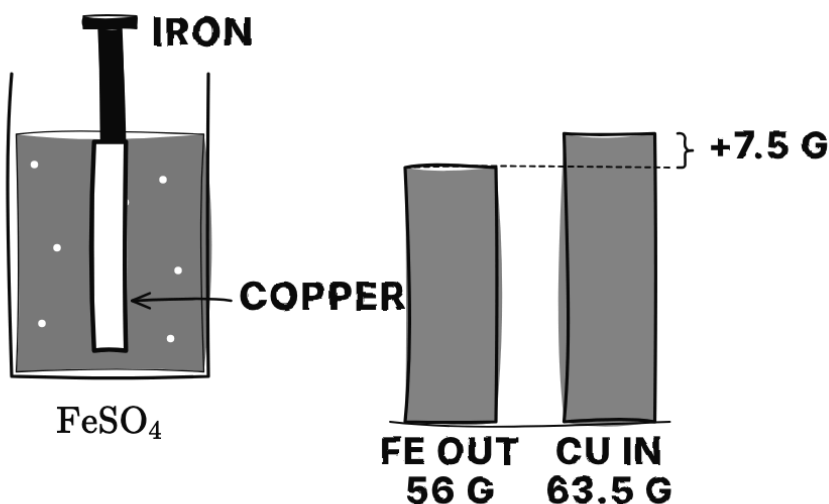
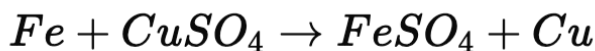


NO ONE NEW, NO ONE LOST

Changing Partners

His example you can almost see. Dissolve blue vitriol, which is copper sulphate, in water to get a clear blue liquid, and dip an iron nail into it. After a while the nail is coated with red copper, and the liquid contains green vitriol, iron sulphate, which differs from the blue one only in that iron has taken the place of copper. In today's notation the reaction is $\text{Fe} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}$. Match it to the letters: B is the iron, Fe; A is the copper sulphate, so D is the copper, Cu, and E is the sulphate part, SO_4 ; and C, the sulphate now joined to iron, is the iron sulphate. A small calculation shows that the dance keeps every dancer. In modern units, 56 grams of iron take the place of 63.5 grams of copper, so if 56 grams of iron dissolve, 63.5 grams of copper come out of the solution onto the nail. The nail grows heavier by the difference, 7.5 grams, while the solution grows lighter by exactly the

same amount. Mendeleev notes that iron can be coated with copper and copper with silver in this way, and that such reactions are used all the time. Electroplating in a modern workshop, where a dull metal object comes out of a bath with a shiny coat, rests on the same exchange of partners.

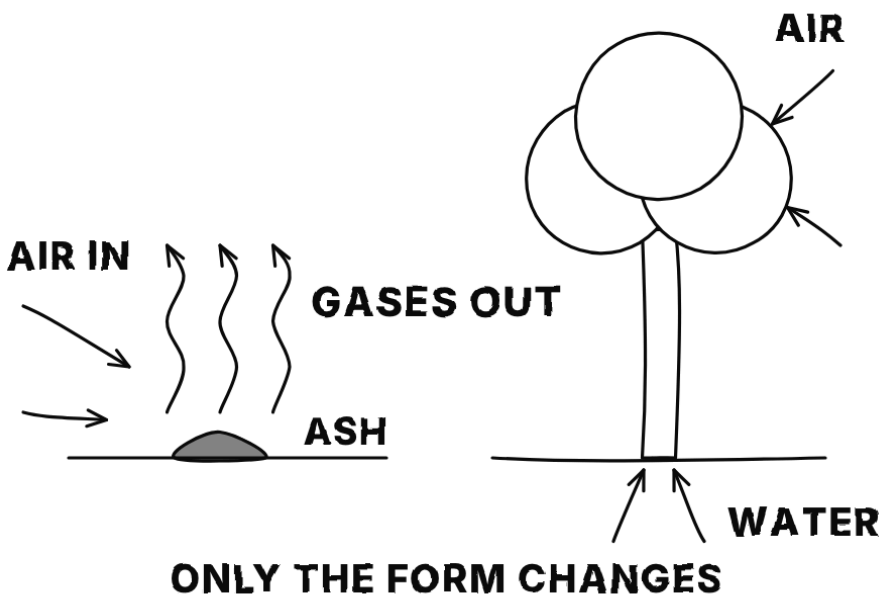


Iron Takes Copper's Place

Why, then, did chemistry arrive so late, when people had smelted metals, baked bread and brewed beer for thousands of years? Mendeleev gives two reasons. The first is complexity: most reactions in nature and in factories are many combinations, decompositions and substitutions going on at once, so nobody could predict or control them. The second is gases, above all air. Only in the sixteenth and seventeenth centuries did people understand that air has weight, and

that a gas is a state of matter that is springy and spreads out in all directions. Before that, gases slipped through every account, because they could not be seen.

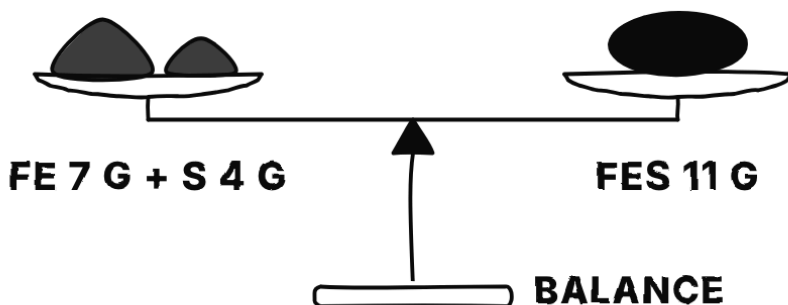
And this brings us back to the fireplace. Wood burns and leaves a little ash, so matter seems to vanish. A tiny seed grows into a huge tree, so matter seems to be created out of nothing. Both impressions come from the same mistake: forgetting the invisible gases. When wood burns, it turns into gases that 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 you find something surprising: they weigh more than the wood did. The extra weight is a part of the air that the burning wood has taken up, just as iron grows heavier when it rusts. Gunpowder does not vanish either; it becomes powder gases and smoke. And the tree is built from gases taken from the air, together with water and dissolved substances drawn up by its roots; put a plant in a gas without the nourishing part of the air, and it does not grow but dies. Water that dries from a wet cloth comes back as rain, dew and snow, and water that sinks into the ground comes out again as springs.



The Invisible Gases

Mendeleev draws the conclusion in a single sentence that deserves to be quoted. Matter, in all its physical and chemical changes, "only changes its place and form, but is neither lost nor created." Some Greek philosophers had guessed this, and in the seventeenth century so had Mariotte, but nobody stated it clearly or used it. The man who proved it, in the second half of the eighteenth century, was Antoine Lavoisier, a French academician who also worked as a tax farmer, collecting taxes for the crown, and whom Mendeleev calls the founder of modern chemistry. His tool was the balance, the only instrument, as Mendeleev says, that measures the quantity of matter directly and exactly. Lavoisier weighed everything that went into an experiment, even the vessels, and everything that came out. Every time, the total weight after the reaction was equal to the total weight before it.

$$7 + 4 = 11$$



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

What Goes In Comes Out

Here is that law as a formula, which Mendeleev is about to write down. Call the weights of the substances taken A, B, C and so on, and the weights of the substances produced M, N, O and so on. Then $A + B + C + \dots = M + N + O + \dots$. In words: the left-hand side is everything you put in, the right-hand side is everything you got out, and the two are equal. The intuition is bookkeeping: no item may appear in the books or disappear from them without a record, so the totals must agree. Take the iron and sulphur from before as a calculation aloud. Seven grams of iron heated with four grams of sulphur give, when they combine completely, eleven grams of iron sulphide, because $7 + 4 = 11$. If you weighed ten grams afterwards, you would not conclude that a gram had vanished; you would look for what escaped, or for what you had failed to collect. A kitchen scale is enough to feel this:

weigh a sealed jar with baking soda and vinegar inside before and after they fizz, and the reading does not change, because the gas stays inside the jar.

Mendeleev is careful about the words. "Matter is eternal" and "mass is conserved" are short phrases, and they contain a hypothesis. What has actually been seen is longer and more modest: in every experiment and every natural process studied, the weight of the products has never been found to be greater or smaller than the weight of the starting substances, within the accuracy of weighing. Because weight is proportional to mass, the amount of matter, this means that nobody has ever seen matter disappear or appear anew. And this law gives chemistry its precision, because it lets you write an equation for every reaction and check it on the balance.

Try it yourself

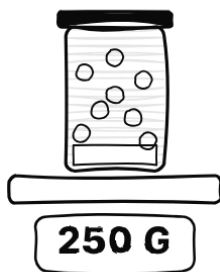
Take a small glass jar with a screw lid, put a spoonful of baking soda in it, and stand a tiny cup of vinegar inside so that the two do not touch yet. Close the lid tightly and weigh the whole jar on a kitchen scale. Now tip the jar so the vinegar pours onto the soda, and watch it fizz while the lid stays closed. Weigh the jar again: the reading is the same as before. Then open the lid, let the gas out, close it and weigh once more: now the jar is a little lighter, because the invisible gas, which had weight, has left.

BEFORE



=

FIZZED



OPENED



The Sealed Jar Test

Remember

Chemistry studies substances that are the same all through and how they turn into one another, driven by forces hidden in their smallest particles. Reactions come in three main kinds: combination, where several substances become fewer; decomposition, where one becomes several; and substitution, where parts change partners, as when iron takes the place of copper. Matter only seemed to vanish in fire or appear in a growing tree because the invisible gases were left out of the account. Lavoisier, using the balance, showed that the total weight after a reaction always equals the total weight before it. That equality lets chemists write an equation for every reaction, and it is the foundation of chemistry as an exact science.

Questions

1. In the letter scheme $DE + B \rightarrow EB + D$, what makes this a substitution rather than a combination or a decomposition?
 - a. Two substances go in and two come out, with the part E moving from D to B
 - b. Two substances go in and one comes out, so they have joined together
 - c. One substance goes in and two come out, so it has fallen apart
 - d. The substances go in and come out unchanged, only mixed

2. Smoke from burning wood, collected and weighed, turns out heavier than the wood. What follows?
 - a. Burning creates a little new matter
 - b. The ash must have been lighter than it seemed
 - c. The wood has taken up a part of the air while burning
 - d. Smoke is denser than wood, so it always weighs more
3. You heat a weighed mixture of iron and sulphur and find the product weighs less than the two together. What does the law of conservation tell you to do?
 - a. Conclude that some matter was destroyed by the heat
 - b. Accept the loss as normal for combinations
 - c. Conclude that the balance is not needed in chemistry
 - d. Look for something that escaped or was not collected
4. Why could chemistry not become an exact science before people understood that gases have weight?
 - a. Because reactions only happen in gases
 - b. Because the gases taken in or given off were left out of every account, so the weights never matched
 - c. Because gases could not be heated in the vessels of the time

Answers

1. **a)** The part E has moved from one partner to another and D has been left on its own; it is a decomposition and a combination happening together, two giving two.
2. **c)** The extra weight is a part of the air that the burning wood has taken up, just as iron grows heavier when it rusts.

- 3. d)** Since the total weight after a reaction always equals the total before, a missing gram means something escaped or was left out of the account.
- 4. b)** Before the sixteenth and seventeenth centuries gases slipped through every account because they could not be seen, so matter seemed to vanish or appear.

Worked examples

Iron and sulphur on the balance Seven grams of iron are heated with four grams of sulphur, and they combine completely into iron sulphide. What does the iron sulphide weigh?

Write the law of conservation: the weights taken add up to the weights produced, $A + B = M$.

The substances taken are the iron, $A = 7$ grams, and the sulphur, $B = 4$ grams.

The combination is complete, so the only product is the iron sulphide, with weight M .

So $M = 7 + 4 = 11$ grams.

Answer: 11 grams

Practice

1. A sealed jar with baking soda and a small cup of vinegar weighs 250 grams. The vinegar is tipped onto the soda and fizzes with the lid closed; then the lid is opened, the gas lets out, and the jar now weighs 248 grams. What did the jar weigh with the lid still closed after fizzing, and how much gas escaped?

Hint: With the lid closed nothing could leave, so apply $A + B + \dots = M + N + \dots$ to everything inside the jar.

Answer: With the lid closed it still weighed 250 grams, because nothing was gained or lost. After the gas left it weighed 248 grams, so the gas that

escaped weighed $250 - 248 = 2$ grams.

2. Iron dipped into copper vitriol gives copper and iron vitriol. Using the scheme $DE + B \rightarrow EB + D$, say which substance plays each letter, and explain why the reaction counts as a substitution.

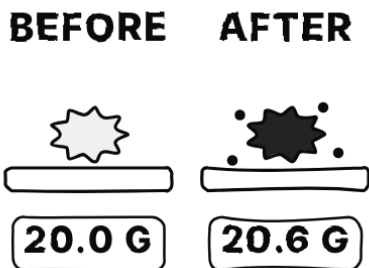
Hint: B is what you dip in; D is what comes out on its own.

Answer: B is the iron, A or DE is the copper vitriol, D is the copper set free, E is the rest of the vitriol, and C or EB is the iron vitriol. Two substances give two new ones, and iron has simply taken the place of copper, so it is a substitution, or double decomposition.

What the Balance Notices

Leave a steel wool pad in a damp sink overnight, and in the morning it is orange with rust. Most people would say the iron has been eaten away, that something has been taken from it. Now put the same pad on a precise scale before and after rusting. It has become heavier. Something has been added, not taken, and only the scale could tell you so. The scale in a chemistry lab that reads to a thousandth of a gram is the modern heir of the balance this part is about.

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



ORANGE RUST



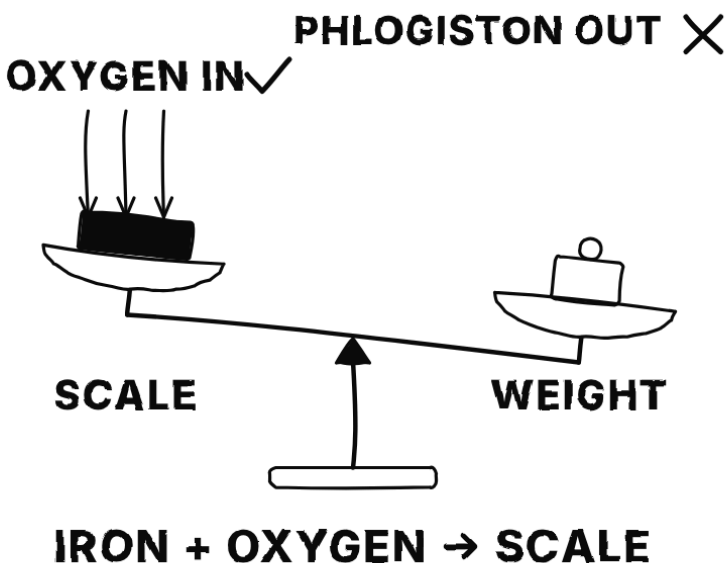
$$10 = 6.4 + X$$

$$X = 3.6 \text{ G}$$

The Balance Finds a Hidden Weight

Mendeleev starts from the equation of the last part, the law of conservation written in letters: $A + B + C + \dots = M + N + O + \dots$. On the left stand the weights of the substances taken, on the right the weights of the substances produced. He points out two things this equation does for a chemist. First, if one weight in it is unknown, you can find it, because everything else is known and the two sides must balance. Second, it is an alarm bell: if you forget one of the substances, the sums will not agree, and you will notice at once. Here is the first use as a calculation aloud. Suppose you heat 10 grams of a substance, and it leaves 6.4 grams of a solid while a gas escapes unseen. The equation reads $10 = 6.4 + x$, where x is the weight of the gas. So $x = 10 - 6.4 = 3.6$ grams. You have weighed a gas you never saw, simply by trusting the balance. Mendeleev says a beginner must become fully at home with this simple truth, and gives examples.

The first is iron. Iron rusts in damp air, and when it is heated strongly in air it becomes coated with scale, a dark flaky crust. Rust and scale are both earthy substances, much like the iron ores dug from the ground to make iron. Weigh the iron before and after, and you find that its weight has grown. Lavoisier showed where the extra weight comes from: from the part of the air called oxygen, the part that serves for burning. The proof is simple: in a vacuum, or in gases without oxygen, such as hydrogen or nitrogen, iron neither rusts nor forms scale. So by the law of conservation, the gain in weight tells you that scale is more complex than iron, and that making it is a combination: $\text{iron} + \text{oxygen} \rightarrow \text{scale}$.

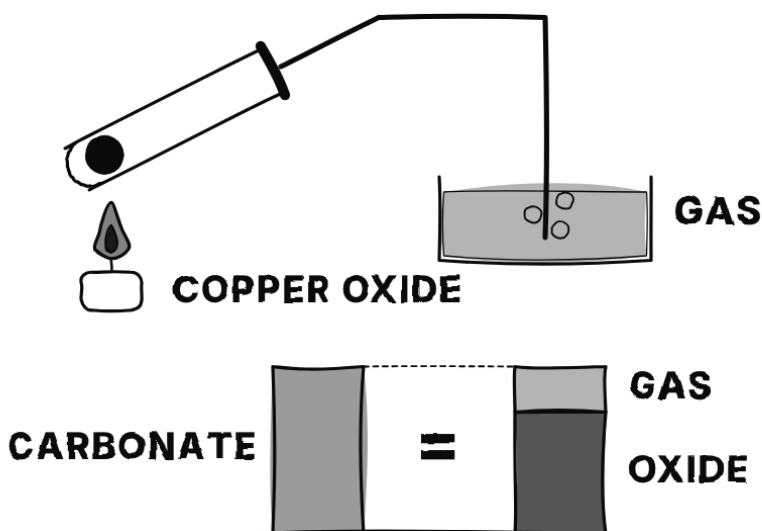


Iron Plus Oxygen, Not Minus Phlogiston

Without the balance, Mendeleev says, it was easy to read this backwards. Before Lavoisier, chemists thought scale was the simpler body and iron the more complex one. Iron, they said, contained a special invisible substance called phlogiston, and when iron turned into scale it lost its phlogiston. That story sounds reasonable until you weigh things: something that loses a part should become lighter, yet the scale is heavier. Phlogiston was an imaginary substance, and the balance was what showed that the story ran the wrong way.

The second example is the green copper compound that Mendeleev promised to describe. Copper carbonate is sold as a green powder, and the green stone malachite, used for ornaments and as a copper ore, contains it. Heat either, and it turns into a black powder called

copper oxide, which is also the scale that forms on copper heated in air. This time the black powder weighs less than the green powder did. The law of conservation tells you at once what that means: something has left, so this is a decomposition. To catch what left, close the heated vessel with a tight cork and pass a bent tube through it, with its far end under water. As the green powder darkens, bubbles stream out of the tube through the water. Collect that gas, and a burning splinter dipped into it goes out as if dipped into water. It is carbonic acid gas, the same gas that limestone gives off when heated, and we now call it carbon dioxide. Mendeleev's point is that this gas is clear and colourless, just like air, so without the balance nobody would have suspected it was there. And when it is weighed too, the black copper oxide plus the gas add up exactly to the green powder you started with.



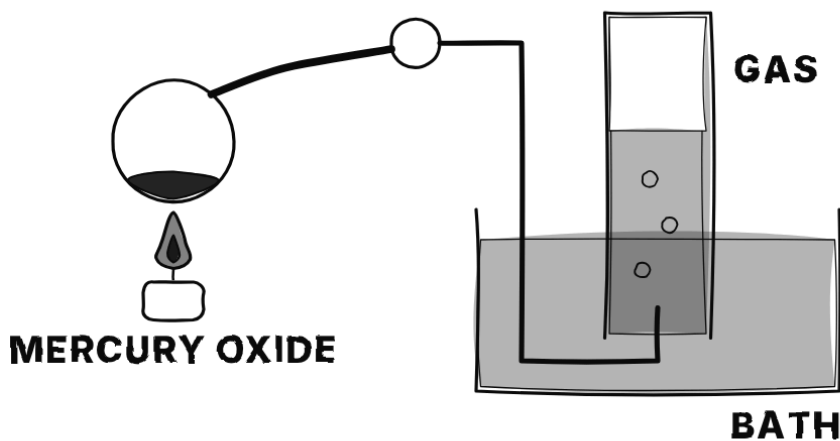
The Gas the Eye Misses

Try it yourself

Put a spoonful of baking soda in a small heat-proof jar and weigh it on a kitchen scale. Heat the jar gently in an oven for half an hour, let it cool, and weigh it again. The jar is lighter, although nothing visible has left it. Like the green copper powder, the soda has given off gas and water vapour, and the balance has noticed what your eyes could not.

The third example, Mendeleev says, matters more than any other for the history of chemistry. It is red mercury oxide, a red powder that forms as the scale of mercury when mercury is heated in air. Picture

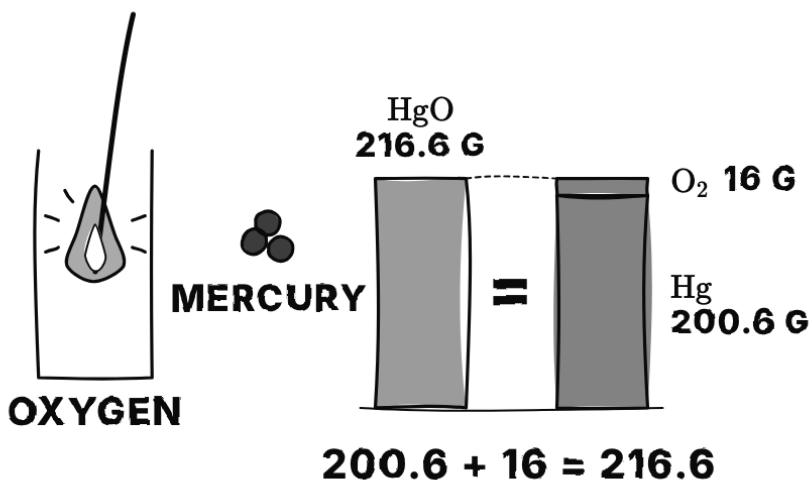
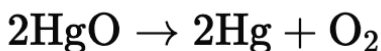
the apparatus he draws. A glass retort, a bulb with a long neck, holds the red powder over a flame. Its neck is pushed through a tight cork into a small glass ball, and from the other side of the ball a tube runs down and dips into a tub of water, called the bath. Any gas that forms has only one way out: through the tube and up through the water as bubbles.



Catching a Gas Under Water

Now the clever part, the way to catch a gas. Fill a tall glass cylinder to the brim with water, stop its mouth, turn it upside down, and put the mouth under the water of the bath before you unstop it. The water stays up in the cylinder, held by the pressure of the air on the bath. Set the cylinder over the end of the tube, and every bubble that comes out rises into it and pushes some water down. When you heat the

retort, first comes ordinary air, expanding in the heat, and then a new gas. Close the cylinder under water, lift it out, turn it mouth upwards, and lower a glowing splinter into it, one that is only smouldering. In air such a splinter quietly dies out; in this gas it bursts into a bright flame. This is oxygen, and the flaring splinter is still how chemists recognise it. At the same time, shiny drops of metallic mercury appear on the cool parts of the retort and in the ball, like a silver mirror. So one red powder gave two new bodies, mercury and oxygen: a decomposition.

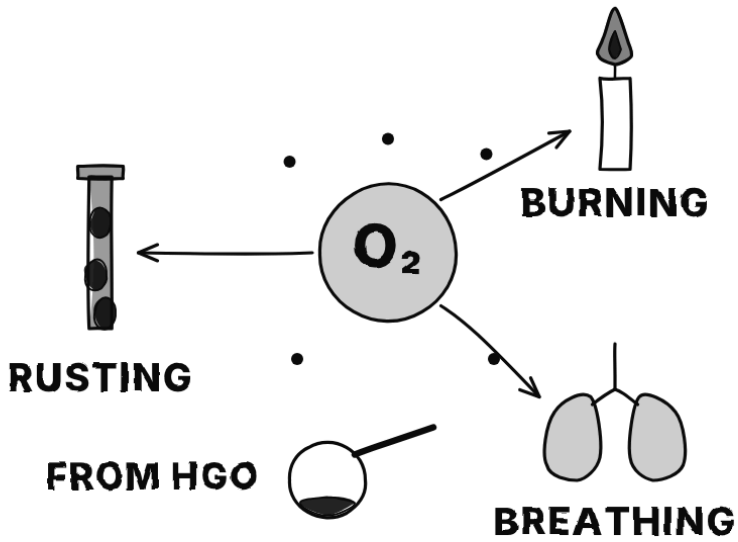


$$216.6 = 200.6 + 16$$

Let us put it on the balance with modern numbers, as a calculation aloud. In today's notation the reaction is $2\text{HgO} \rightarrow 2\text{Hg} + \text{O}_2$. In words: red mercury oxide breaks into mercury and oxygen gas.

Measured in grams, about 216.6 grams of red mercury oxide give about 200.6 grams of mercury and 16 grams of oxygen. Check the books: $200.6 + 16 = 216.6$. Nothing appeared and nothing vanished; the oxygen simply went where the eye could not follow it.

Why was this experiment so important? People before Lavoisier could already collect and study gases, but he was the first to show what part they played in reactions that had been misunderstood or merely watched. The gas from red mercury oxide is the same oxygen that is in the air. It is the gas that animals breathe, the gas that fuels burning, and the gas that turns metals into rusts and scales, which chemists of that time called calxes, earthy substances like the ores metals come from. So with one red powder, a flame and a balance, the whole picture of rusting, burning and breathing came into focus: each one is a combination with oxygen from the air.



One Gas Behind Three Changes

Remember

The law of conservation lets a chemist find an unknown weight, and it warns at once if a substance has been left out of the account. Iron grows heavier when it rusts or forms scale, so scale is iron combined with oxygen, not iron that has lost phlogiston. Green copper carbonate grows lighter when heated because it gives off invisible carbonic acid gas, and the two products together weigh as much as the powder did. Red mercury oxide, heated, gives mercury and oxygen, a gas in which a glowing splinter bursts into flame. That oxygen is the part of the air behind burning, breathing and rusting, and the balance is what revealed it.

Questions

1. A chemist adds up the weights before and after a reaction and the two sums do not agree. What does the law of conservation tell them?
 - a. That this reaction creates or destroys a little matter
 - b. That one of the substances taken or produced has been left out of the account
 - c. That the balance must be broken and the result can be ignored
 - d. That the reaction was a combination rather than a decomposition

2. Why does the experiment in a vacuum, or in hydrogen or nitrogen, matter for understanding rust and scale?
 - a. Because iron rusts faster there, which shows the air slows rusting
 - b. Because it shows the extra weight comes from the moisture in the iron
 - c. Because without the oxygen of the air no rust or scale forms, so the extra weight must come from oxygen
3. Green copper carbonate becomes black copper oxide and weighs less. What kind of reaction is it, and how do you know?
 - a. A decomposition, because the loss of weight shows that something has left
 - b. A combination, because the colour has changed
 - c. A substitution, because copper has changed partners
 - d. A combination with oxygen, as with iron scale
4. A glowing splinter is lowered into the gas collected from heated red mercury oxide. What happens, and what does it tell you?
 - a. It goes out, which shows the gas is carbonic acid gas
 - b. It glows exactly as in air, which shows the gas is only expanded air
 - c. It turns silver, which shows mercury vapour is present
 - d. It bursts into a bright flame, which shows the gas is oxygen

Answers

1. **b)** The equation is an alarm bell: if you forget one of the substances, the sums will not agree, and you notice at once.

- 2. c)** In a vacuum or in gases without oxygen iron neither rusts nor forms scale, so the gain in weight comes from the oxygen of the air.
- 3. a)** The law of conservation tells you at once that if the product is lighter, something has left, so this is a decomposition; the escaping gas can be caught as bubbles.
- 4. d)** In air such a splinter quietly dies out; in this gas it bursts into a bright flame, and that is how oxygen is recognised.

Worked examples

Weighing a gas you never saw Some green copper carbonate weighing 12.4 grams is heated until it has all turned into black copper oxide, which weighs 8.0 grams. The gas escapes unseen. How much gas was given off?

Write the law of conservation: the weight taken equals the sum of the weights produced, $A = M + N$.

The substance taken is the copper carbonate, $A = 12.4$ grams.

The products are the copper oxide, $M = 8.0$ grams, and the gas, N , which is unknown.

So $12.4 = 8.0 + N$, and $N = 12.4 - 8.0 = 4.4$ grams.

Answer: 4.4 grams of gas

Practice

1. An iron nail weighing 20 grams is heated strongly in air until it is partly covered with scale. It now weighs 21.5 grams. How much of the air combined with it, and which part of the air was it?

Hint: The iron and the part of the air taken together must weigh as much as the scaled nail.

Answer: 1.5 grams, since $20 + x = 21.5$ gives $x = 1.5$. It was oxygen, the part of the air that serves for burning, because without oxygen no scale forms.

2. A follower of the phlogiston theory says that when iron turns into scale it gives up phlogiston. Using the balance, explain why this story runs the wrong way.

Hint: If something leaves the iron, what should the balance show?

Answer: If the iron lost something, the scale would weigh less than the iron. The balance shows it weighs more, and no scale forms without oxygen. So something has been added: scale is iron combined with oxygen, a more complex body than iron, not a simpler one.

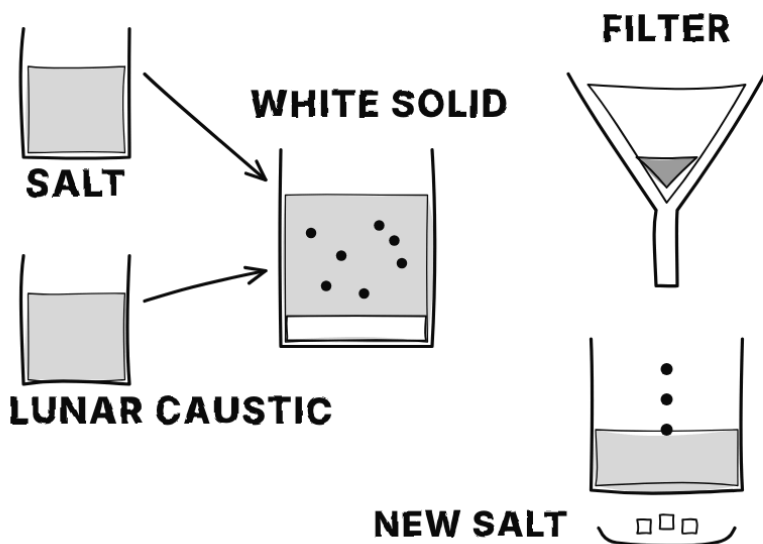
3. Red mercury oxide is heated in a closed retort whose tube leads into the water bath, and both the mercury droplets and the collected gas are weighed. What should the two weights add up to, and why?

Hint: Count everything that went in and everything that came out of the retort.

Answer: They should add up to the weight of the red mercury oxide taken. One body decomposed into two, mercury and oxygen, and since nothing is created or lost, the two together must weigh as much as the powder did.

Salt, Silver and the Alchemists' Mistake

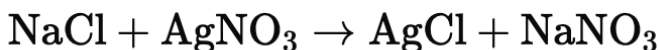
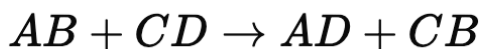
Take two glasses of water that look exactly alike, perfectly clear. In one, common table salt is dissolved; in the other, a silver salt called lunar caustic, which doctors once used to burn and clean wounds. Pour one glass into the other. At once the liquid turns milky white, and soon a white powder settles to the bottom. Two clear liquids have made something solid, and the question is what happened to the weight.



Two Clear Liquids, One White Solid

Mendeleev uses this as one more example of the law of conservation. First he separates the powder from the liquid by filtering. Fold a circle of unsized paper in four, open it into a cone, and set it in a glass funnel. Pour the milky liquid in: a clear solution runs through, and the white powder stays on the paper. It is the same thing a coffee filter does in your kitchen, where the liquid runs through and the grounds stay behind. Dry the powder, and you find it is a new substance, quite unlike either of the two you started with, because it will not dissolve in water at all. Now boil away the clear liquid that ran through, and another new substance appears, different from both table salt and lunar caustic, though it does dissolve in water like them.

So two substances went in and two came out. This is the third kind of reaction from the first part, a substitution, or double decomposition, where the parts change partners. In letters, two compounds swap their parts, $AB + CD \rightarrow AD + CB$: both partners are exchanged, and two new substances come out. In today's notation, with table salt as NaCl and lunar caustic as AgNO_3 , the reaction reads $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$. In words: the silver leaves its partner and joins the chlorine of the salt, making silver chloride, the white powder; the sodium of the salt takes the place the silver left, making sodium nitrate, which stays dissolved. The intuition is the dance again: the dancers swap partners, and one of the new couples happens to be unable to stay in the water, so it sinks. And the water itself only served to make the substances liquid and mobile, so that their particles could meet as closely as a reaction needs.

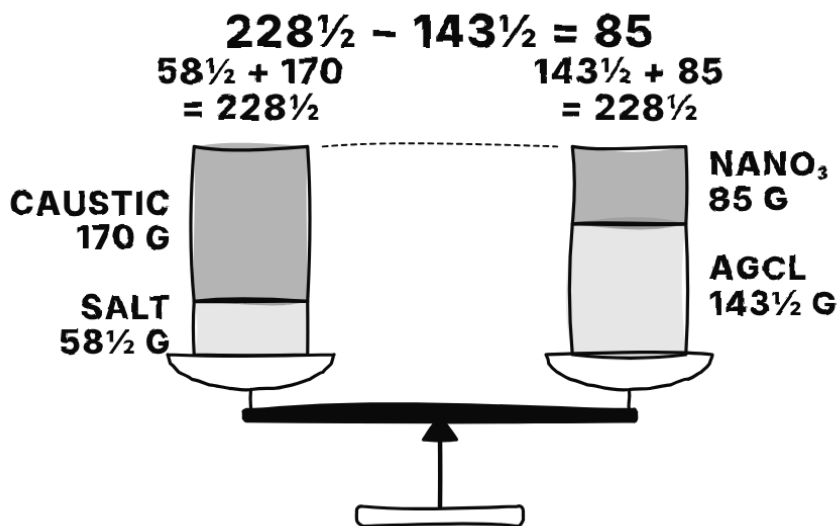


AgCl **SINKS**

NaNO_3 **STAYS DISSOLVED**

Both Partners Change

Now the balance. Mendeleev gives the numbers: about $58\frac{1}{2}$ grams of dry salt and 170 grams of dry lunar caustic give $143\frac{1}{2}$ grams of silver chloride and 85 grams of sodium nitrate. Let us check them aloud. On the left, $58\frac{1}{2} + 170 = 228\frac{1}{2}$ grams. On the right, $143\frac{1}{2} + 85 = 228\frac{1}{2}$ grams. The two sums agree, exactly as the law of conservation demands. And notice what that lets you do. If you had weighed the powder on the filter but spilled the clear liquid, you could still say how much sodium nitrate was in it: $228\frac{1}{2} - 143\frac{1}{2} = 85$ grams. A water-testing lab still works this way: it adds a silver salt to a sample, filters off the white silver chloride, dries it and weighs it to learn how much salt the water held.

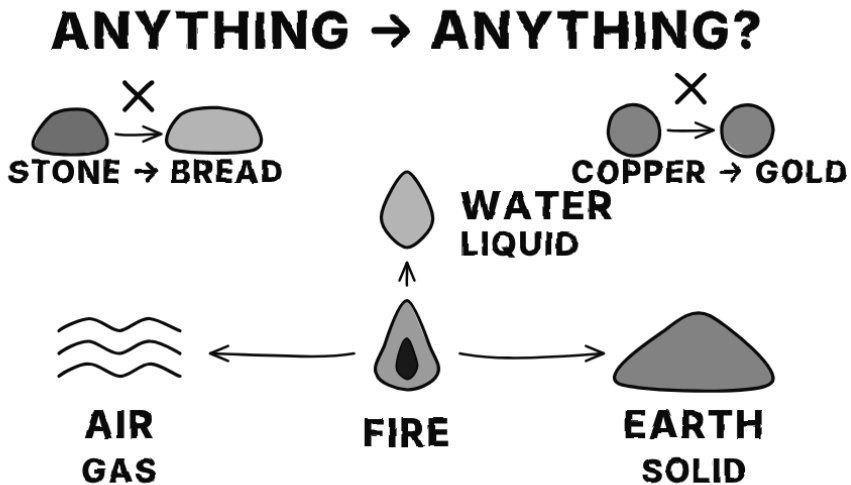


228½ on Both Sides

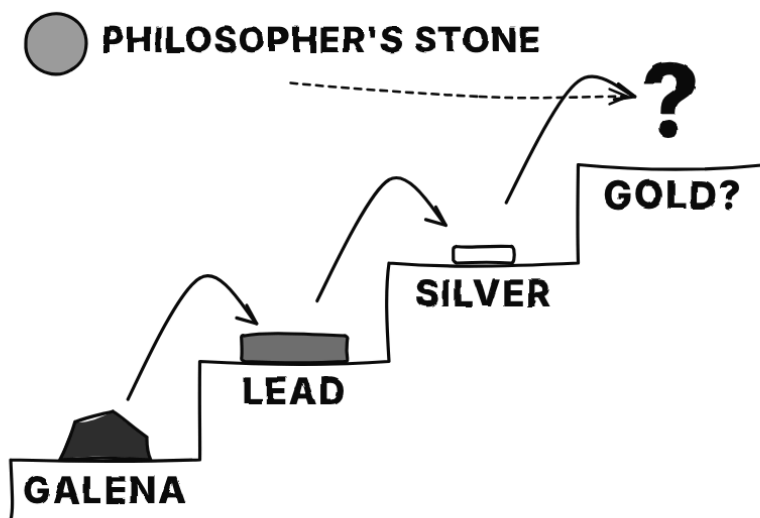
Try it yourself

Dissolve a teaspoon of Epsom salt in one glass of warm water and a teaspoon of washing soda in another, and stir until both are clear. Pour one into the other and watch: the mixture turns cloudy, and a white powder slowly settles. Pour the mixture through a coffee filter; the liquid runs through clear, and a white paste stays on the paper. Just as in Mendeleev's experiment, two clear solutions have exchanged partners and made one substance that cannot stay dissolved.

Here Mendeleev turns to a deeper question. The law of conservation answers the question of quantity: matter is never lost or gained. But there is a second question, which he calls the question of quality, and it is harder. Is there a limit to what one substance can be turned into? Could you, given enough cleverness, turn a pound of anything into a pound of anything else? Looking around does not settle it. Plants make endless different substances from air and soil, and iron can be turned into ink or into the deep blue paint called Prussian blue, so it seems there is no end to the changes. Yet everyday experience says that you cannot make food out of stone, or gold out of copper. Only study can decide.



For a long time the most common answer was the four elements: air, water, earth and fire. The idea came from Asia to the Greeks and was set out most fully by Empedocles, about 460 years before Christ. It was not the result of careful experiments; it seems to have come from sorting things into gases like air, liquids like water and solids like earth, and from seeing that fire, that is heat, changes them. Then Arab scholars began to attack the question by experiment, and through Spain they brought into Europe a passion for such research. It was thought a secret, mysterious science, and it was called alchemy.

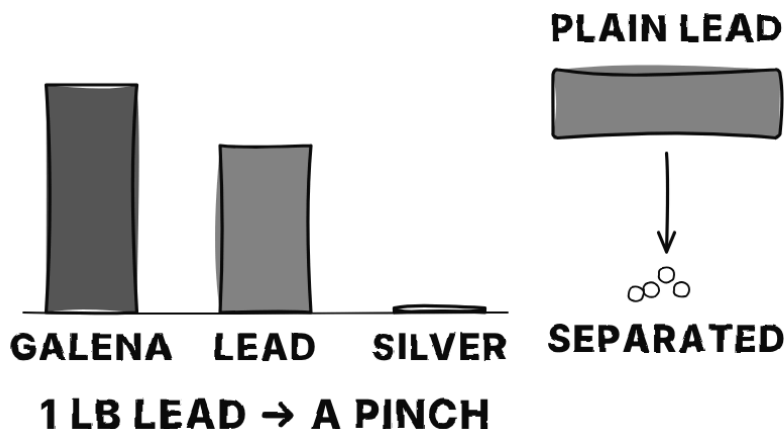


The Alchemists' Ladder

The alchemists believed that the transformations of matter had no limit. They searched for the philosopher's stone, which was supposed to turn anything into gold and diamonds and even to make an old

body young. Mendeleev is fair to them. Their great merit, he says, is that they made a vast number of experiments and discovered many new transformations, and their belief did not come from fantasy alone. Their own experiments seemed to point that way. They took galena, a shiny metallic stone, and got lead from it: a useless stone had become a useful, soft metal. Then they took that lead and got silver from it, a still more precious metal. What could be more natural than to think that one more step would turn the silver into gold?

Their mistake was that they hardly ever weighed. Judgements of quality, such as more noble or more precious, are subjective; quantities are not. Had they weighed, they would have seen that the lead weighs much less than the galena it came from, and that the silver is a tiny amount compared with the lead used. Had they studied the process closely, they would have found that lead does not turn into silver at all. Natural lead simply contains a little silver, and once that silver has been taken out, no further treatment of the lead will give any more. The silver was in the lead all along; it was not made from it. Mendeleev adds that even in his day most of the world's silver was extracted from natural lead in this way.



The Silver Was Inside

So the balance answers the alchemists as clearly as it answered the phlogiston chemists. If lead really turned into silver, a pound of lead would give about a pound of silver, as the law of conservation requires; instead it gives a tiny pinch, and then nothing more. That small number is the whole argument: what came out was hidden inside from the start.

Mendeleev's verdict on alchemy is short. The road the alchemists took could never lead to full success, because they did not ask themselves simple, clear questions which, once answered, would let them move on. They asked for everything at once, a stone to make gold and youth, and so they found not one exact law. And yet they left chemistry a rich inheritance: a great store of experimental facts, which later chemists,

asking narrower questions with a balance in hand, could finally put in order.

Remember

Mixing solutions of table salt and lunar caustic gives insoluble silver chloride, which can be filtered off, and sodium nitrate, which stays in solution: a substitution in which two give two. Mendeleev's numbers, $58\frac{1}{2}$ and 170 grams in, $143\frac{1}{2}$ and 85 grams out, both add to $228\frac{1}{2}$ grams, just as the law of conservation requires. Besides the question of quantity there is the question of quality: whether one substance can be turned into any other. The alchemists believed it could, because they got lead from galena and silver from lead, but they rarely weighed. Weighing shows that the silver was already in the lead, and the lesson is that progress comes from simple, clear questions and the balance.

Questions

1. After filtering, the white powder will not dissolve in water. Why does that show it is a new substance?
 - a. Because table salt and lunar caustic both dissolve in water, so a substance that does not cannot be either of them
 - b. Because every powder that settles is a new substance
 - c. Because filtering always changes a substance
 - d. Because it is heavier than the liquid

2. In the salt and lunar caustic experiment, what part does the water play?
 - a. It reacts with the salt to make the white powder
 - b. It is part of the weight on both sides of the equation
 - c. It only makes the substances liquid and mobile, so their particles can meet
3. The alchemists got silver from lead. What would weighing have shown them?
 - a. That lead gains weight as it turns into silver
 - b. That the silver is a tiny amount compared with the lead used, and none more comes once it is taken out
 - c. That lead and silver weigh exactly the same
 - d. That the silver weighs more than the galena it came from
4. According to Mendeleev, why could the alchemists' road never lead to full success?
 - a. Because they had no furnaces hot enough
 - b. Because the four elements made their experiments impossible
 - c. Because they kept their science secret
 - d. Because they did not ask simple, clear questions which, once answered, would let them move on

Answers

1. a) Both starting substances dissolve in water; the powder does not, so it is quite unlike either of the two you started with.
2. c) The water itself only served to make the substances liquid and mobile, so that their particles could meet as closely as a reaction needs.

3. **b)** The silver is tiny compared with the lead, and once it is taken out no further treatment gives any more: the silver was in the lead all along.
4. **d)** They asked for everything at once instead of simple, clear questions, and so they found not one exact law.

Worked examples

Salt and lunar caustic on the balance About $58\frac{1}{2}$ grams of dry table salt react with 170 grams of dry lunar caustic, giving $143\frac{1}{2}$ grams of silver chloride and 85 grams of sodium nitrate. Check that the law of conservation holds.

Write the law: the weights taken equal the weights produced, $A + B = M + N$.

Weights taken: $58\frac{1}{2} + 170 = 228\frac{1}{2}$ grams.

Weights produced: $143\frac{1}{2} + 85 = 228\frac{1}{2}$ grams.

The water is left out on both sides, because it only made the substances liquid; the two sums are equal.

Answer: Both sides come to $228\frac{1}{2}$ grams.

Practice

1. In the same experiment you weighed the $58\frac{1}{2}$ grams of salt and the 170 grams of lunar caustic, and found 85 grams of sodium nitrate after boiling the clear liquid dry, but the paper with the powder tore and was lost. How much silver chloride had formed?

Hint: Use $A + B = M + N$ with the silver chloride as the unknown.

Answer: $143\frac{1}{2}$ grams. The substances taken weigh $58\frac{1}{2} + 170 = 228\frac{1}{2}$ grams, so the silver chloride is $228\frac{1}{2} - 85 = 143\frac{1}{2}$ grams.

2. Explain in your own words the difference between the question of quantity and the question of quality in chemistry, and which one the

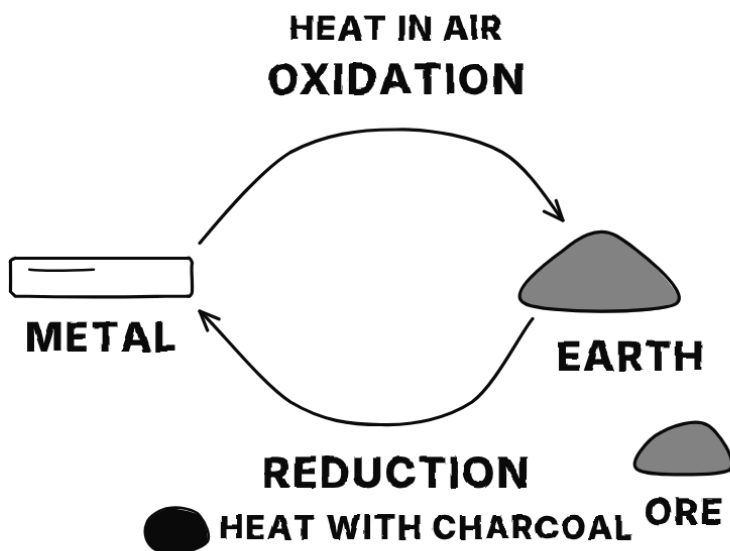
law of conservation answers.

Hint: One asks how much matter there is; the other asks what it can become.

Answer: The question of quantity asks whether the amount of matter changes in a reaction; the law of conservation answers it: matter is never lost or gained. The question of quality asks whether a substance can be turned into any other substance at all; that question is harder and the law of conservation alone does not settle it.

Twelve Days with Mercury

Imagine a glass vessel of shining mercury kept just below the boil, day and night, for twelve days. Slowly, red flakes appear on its surface and spread. At the end, the air shut in with the mercury has shrunk. This experiment, made by Lavoisier in 1774, settled a quarrel that had lasted half a century, and it is the heart of this part.



Oxidation and Reduction

The quarrel was about two transformations that the alchemists had used again and again. Heat a metal such as iron, lead or tin in air, and it turns into an earthy powder: this is oxidation, the same thing as

rusting. Heat that earthy powder with charcoal, and you get the metal back: this is reduction. Many ores in the ground are just such oxidised metals, and tin, iron and copper are won from them by heating with charcoal, as from rust or scale. Every steelworks still runs on this second reaction, reducing iron ore with carbon in a blast furnace. So two transformations were known, one going each way, and explaining them led, as Mendeleev says, to the most important laws of chemistry.

The first explanation came from Becher and above all from Stahl, physician to the King of Prussia, in a book of 1723. In Stahl's picture, every body contains phlogiston, a weightless fiery substance, which he called "the matter or principle of fire, not fire itself". A body that burns or oxidises easily is rich in phlogiston, and charcoal is very rich in it. When a metal oxidises, it gives off its phlogiston; when charcoal reduces the earthy powder, it hands some of its phlogiston back. So for Stahl the metal was the complex body, earth plus phlogiston, and the earthy oxide was the simpler one. The idea was very simple, Mendeleev notes, and partly for that reason it won a great many followers.

STAHL

METAL
→
EARTH
+ PHLOGISTON



AIR GROWS

?

LAVOISIER

METAL
+ PART OF AIR
→
EARTH

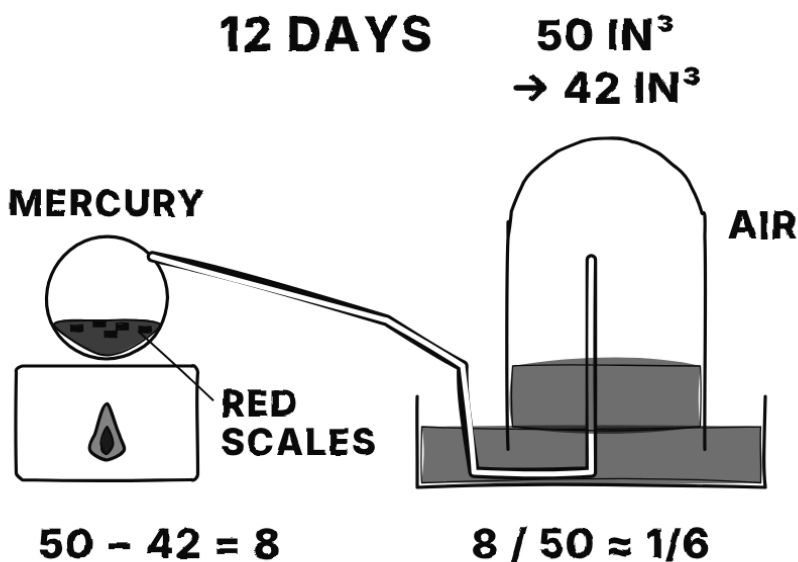


AIR SHRINKS

Two Opposite Pictures

Lavoisier answered with the balance. Every rusting, every oxidation and every burning, he showed, comes with a gain in weight at the expense of the air. And he made the natural assumption that the heavier body is the more complex one. Let us write the two pictures side by side. Stahl: metal → earth + phlogiston. Lavoisier: metal + part of the air → earth. In words: for Stahl something leaves the metal; for Lavoisier something joins it. The two pictures make opposite predictions about the air around the metal. If phlogiston goes out into the air, the air should grow or at least not shrink; if the metal takes part of the air, the air must shrink. So the experiment had one clear question to answer: does the air increase or decrease?

Picture the apparatus. A glass retort, which Mendeleev labels A, holds 4 ounces of pure mercury. Its long neck bends round and dips into a dish of mercury, labelled KS, and its open end O comes up inside a glass bell jar, FQ, standing in that dish. So a fixed amount of air is shut in: the air in the top of the retort and under the bell jar, cut off from the rest of the world by the mercury. Before starting, Lavoisier weighed all the mercury and measured the volume of that enclosed air. That was not easy. He had to know the capacity of the retort, the volume of mercury poured in, the volume of the bell jar up to the mark where the air stood, and the temperature and pressure at the moment of measuring, because a gas swells when warm and shrinks under pressure. Then he heated the retort for twelve days, close to the boiling point of mercury. The mercury grew red scales: it was turning into red mercury oxide, the very powder that gives oxygen when heated more strongly, as we saw.

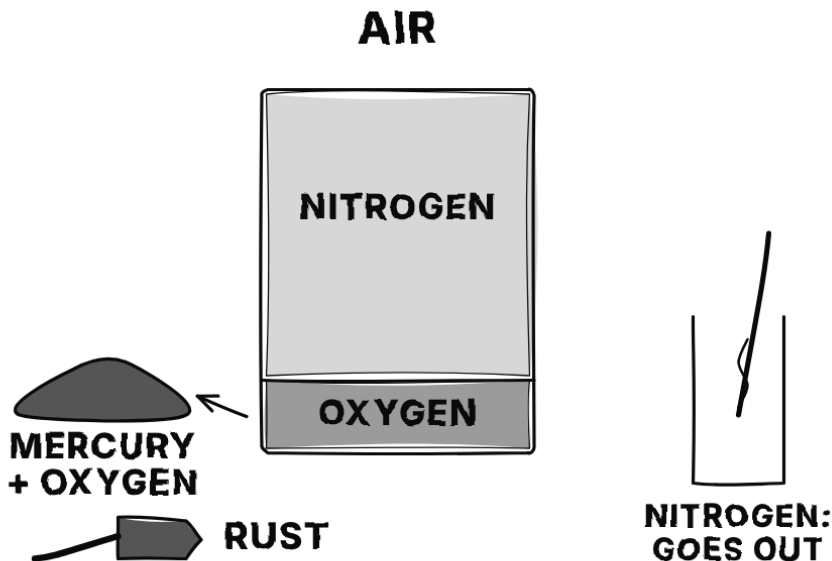


Fifty Shrinks to Forty-Two

When the apparatus had cooled, the air had shrunk. Of 50 cubic inches of air, only 42 were left. Let us read those numbers aloud. The air lost $50 - 42 = 8$ cubic inches. As a share of the air taken, that is $8/50 = 16/100$, about one part in six. Modern measurements put the oxygen in air at about one fifth; Lavoisier's mercury did not take up quite all of it, but the direction was what mattered. The air did not grow, as phlogiston would require; it shrank, and the theory of the German chemist was refuted.

The balance told the rest. The air lost exactly as much weight as the mercury gained. So no part of the air was destroyed: one part of it simply combined with the mercury. That part can be driven back out of red mercury oxide by stronger heat, and it is the gas in which a

glowing splinter bursts into flame: oxygen. The part left behind under the bell jar was quite different. It did not oxidise metals and could support neither burning nor breathing. Lavoisier wrote that a lighted splinter "goes out in it as if dipped into water." This gas we call nitrogen.

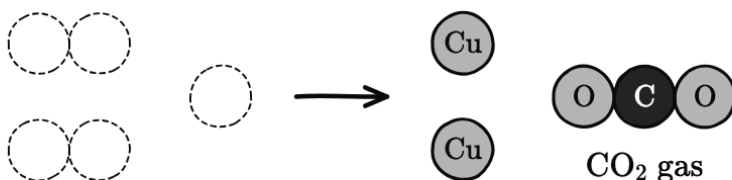
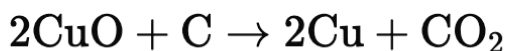


Air Is Oxygen and Nitrogen

So air is not one simple body, as had been believed for two thousand years, but a mixture of two gases, oxygen and nitrogen. Mix the oxygen back with the nitrogen, and you get ordinary air again. Burning and the oxidation of metals take up the oxygen of the air. And the earthy powders made by oxidation are compounds of a metal and oxygen. When you see the brown flakes on an old garden tool, you are

looking at iron that has taken oxygen out of the air, exactly as Lavoisier's mercury did.

One more experiment completed the picture, and it turned reduction around too. When an oxide is heated with charcoal, the oxygen of the oxide passes to the charcoal. What comes off is the very same gas that charcoal gives when it burns in air. In today's notation, for black copper oxide, the reaction is $2\text{CuO} + \text{C} \rightarrow 2\text{Cu} + \text{CO}_2$. In words: two portions of copper oxide hand their oxygen to one portion of carbon; the copper is left bare, and the carbon leaves as carbonic acid gas. In Stahl's picture the charcoal gave something to the earth; in Lavoisier's it takes something from it, and the balance agrees with Lavoisier. And so carbonic acid gas, too, is a compound, of carbon and oxygen, just as oxides are compounds of metals and oxygen.



COPPER LEFT BARE

✗ PHLOGISTON GIVEN

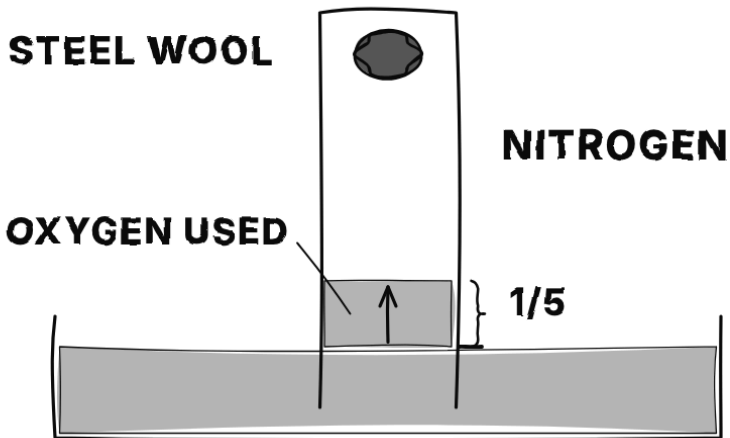
✓ OXYGEN TAKEN

Charcoal Takes the Oxygen

Try it yourself

Wet the inside of a narrow glass jar, push a pad of steel wool to the bottom so it stays put, and stand the jar upside down in a dish of water. Mark the water level inside the jar with a pen. Leave it for two or three days. The steel wool turns rusty, and the water rises up into the jar, because the iron has taken up the oxygen of the enclosed air, just as Lavoisier's mercury did. The water climbs about a fifth of the way up the air space, and what is left above it is mostly nitrogen.

3 DAYS



Steel Wool in an Upturned Jar

Remember

Oxidation turns a metal into an earthy powder; reduction with charcoal turns the powder back into metal. Stahl explained both by phlogiston leaving the metal and coming back from the charcoal, so for him the metal was the complex body. Lavoisier's twelve-day experiment showed that heated mercury takes up part of the enclosed air: 50 cubic inches shrank to 42, and the air lost exactly the weight the mercury gained. Air is a mixture of oxygen, which supports burning and combines with metals, and nitrogen, which supports neither burning nor breathing. Oxides are compounds of metals with oxygen, and in reduction the charcoal takes that oxygen and leaves as carbonic acid gas, itself a compound of carbon and oxygen.

Questions

1. Stahl and Lavoisier made opposite predictions about the air shut in with heated mercury. What did each predict?
 - a. Stahl: the air should not shrink, since phlogiston goes into it; Lavoisier: the air must shrink, since the mercury takes part of it
 - b. Stahl: the air must shrink; Lavoisier: the air should grow
 - c. Both predicted that the air would stay the same
 - d. Stahl: the mercury should get heavier; Lavoisier: the mercury should get lighter

2. Why did Lavoisier need to know the temperature and pressure when he measured the enclosed air?
 - a. Because mercury boils only at one pressure
 - b. Because a gas swells when warm and shrinks under pressure, so the volume could not be compared otherwise
 - c. Because the bell jar might break if it got too hot
3. The air lost exactly as much weight as the mercury gained. What follows?
 - a. That part of the air was destroyed by the heat
 - b. That phlogiston has a negative weight
 - c. That one part of the air combined with the mercury, and nothing was destroyed
 - d. That the mercury turned partly into air
4. When black copper oxide is heated with charcoal, the metal comes back. What happens to the oxygen, in Lavoisier's picture?
 - a. It stays in the copper as phlogiston
 - b. It is destroyed in the heat
 - c. It passes into the air as nitrogen
 - d. It passes to the charcoal, which leaves as carbonic acid gas

Answers

1. a) If phlogiston goes out into the air, the air should grow or at least not shrink; if the metal takes part of the air, the air must shrink.
2. b) He had to know the temperature and pressure at the moment of measuring, because a gas swells when warm and shrinks under pressure.

3. c) No part of the air was destroyed: one part of it simply combined with the mercury.
4. d) The oxygen of the oxide passes to the charcoal, and what comes off is the same gas that charcoal gives when it burns in air.

Worked examples

How much of the air the mercury took Lavoisier shut 50 cubic inches of air in with the mercury; after twelve days of heating only 42 cubic inches were left. How much air combined with the mercury, and what share of the air was that?

The air that combined is what is missing: $50 - 42 = 8$ cubic inches.

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

Multiply top and bottom by 2: $8/50 = 16/100$, so 16 parts in a hundred.

That is about one part in six; the air shrank, as Lavoisier's picture predicts and Stahl's does not.

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

Practice

1. Suppose the same experiment were done with 100 cubic inches of air, and the mercury took up the same share as in Lavoisier's experiment. How much air would be left?

Hint: First find the share taken up, 8 out of 50, and apply it to 100.

Answer: 84 cubic inches. The share taken up is $8/50 = 16/100$, so 16 cubic inches combine with the mercury and $100 - 16 = 84$ remain.

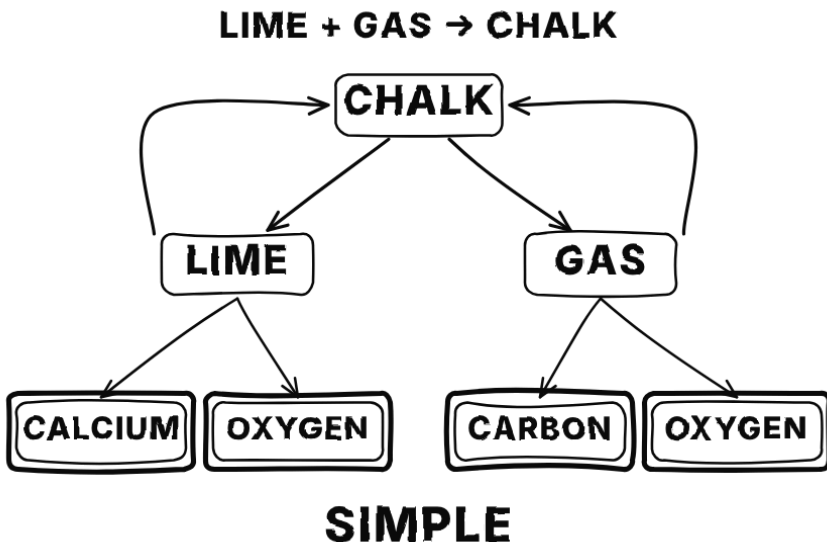
2. A follower of Stahl says charcoal reduces an oxide by giving it phlogiston. Using what happens to the oxygen and to the gas given off, explain Lavoisier's answer.

Hint: Ask what leaves the oxide and where it goes.

Answer: In reduction the charcoal does not give something to the oxide; it takes the oxygen from it. The oxygen passes to the charcoal, which leaves as carbonic acid gas, the same gas charcoal gives when burning in air, so that gas is a compound of carbon and oxygen and the oxide was a compound of the metal and oxygen.

Simple Bodies and the Letters of Chemistry

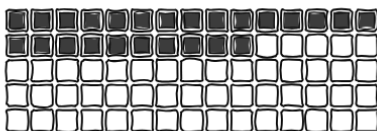
Put a lump of chalk in a hot fire, and it gives off a gas and leaves behind white lime. Now let that lime stand in the same gas, with a little water, at room temperature, and it slowly turns back into something like chalk. So chalk can be taken apart and put together again: it is a compound. The white lime mortar between old bricks hardens in exactly this way, drawing that gas out of the air over months. But are its two parts, the lime and the gas, the end of the road?



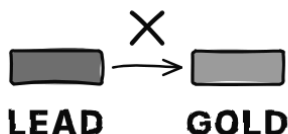
Down to the Simple Bodies

No, says Mendeleev. The gas, carbonic acid gas, is carbon combined with oxygen, as we saw in the last part. And lime is the oxide of a metal called calcium. Keep breaking substances into their parts like this, and at last you reach ones that no possible means can split into two or more others, and that cannot be built up out of anything else. Such substances can only combine with others or act on them. They are called simple bodies, or simple substances, and every homogeneous substance is either simple or a compound. This division goes back to Lavoisier.

The simple bodies are few compared with the compounds they make. In Mendeleev's day about seventy-five were known with certainty, and of these no more than twenty-five turn up in the compounds of everyday life. And simple bodies do not turn into one another. Not a single case had ever been seen, in spite of enormous efforts, so one metal cannot be turned into another, and nobody had found the slightest sign that oxygen, iron or sulphur were really compounds. This is the answer to the alchemists, now in its exact form.

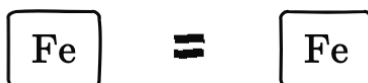


**75 SIMPLE
25 EVERYDAY**



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

FOR EACH SIMPLE BODY



Few, Fixed and Conserved

Put this together with the law of conservation, and something stronger follows. A simple body cannot be decomposed, and matter is never lost or created; therefore the amount of each simple body stays the same through every chemical change. The old equation, $A + B + \dots = M + N + \dots$, now holds not only for the total weight but for every simple body separately. In words: whatever iron went into a reaction comes out as iron, combined with something new, and whatever oxygen went in comes out as oxygen. Chemistry, Mendeleev says, comes down to studying what each simple body is joined to, and how, before and after a change.

To write such equations, chemists agreed on letters. Each simple body gets one or two first letters of its Latin name. Oxygen, Oxygenium, is

O; nitrogen, Nitrogenium, is N; mercury, Hydrargyrum, is Hg; iron, Ferrum, is Fe. A compound is written by putting the letters of its simple bodies side by side, so red mercury oxide is HgO: mercury and oxygen. But the letters carry more than names. Each letter also stands for a fixed weight, which Mendeleev calls the proportion, or the weight of the atom. So a formula tells you not only what a compound is made of but how much of each, and in every equation built from formulas the weight of each simple body must be the same on both sides.

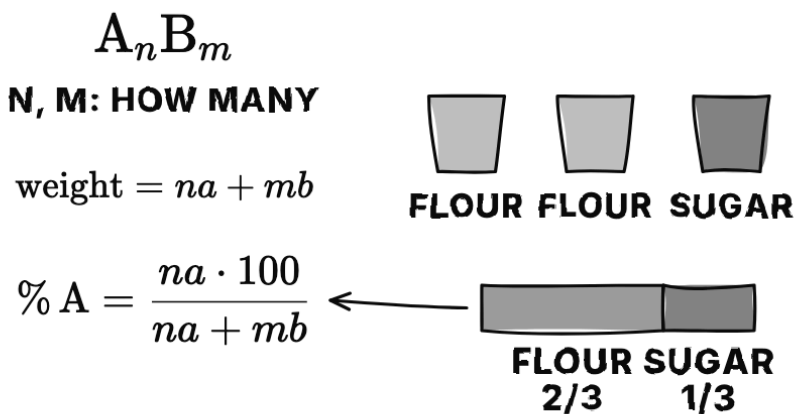
O	OXYGENIUM		
N	NITROGENIUM		
Hg	HYDRARGYRUM		HgO
Fe	FERRUM		RED OXIDE

ATOM WEIGHTS

Letters for the Simple Bodies

Now the formula that this part is really about. A compound of two simple bodies, A and B, is written A_nB_m , where n and m say how many proportions of each go into it. Call the atomic weight of A a, and that

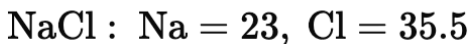
of B b. Then one unit of the compound holds na of A and mb of B, and weighs $na + mb$ in all. So in every hundred parts of the compound, the share of A is $na \cdot 100 / (na + mb)$, and the share of B is $mb \cdot 100 / (na + mb)$. In words: the part of A divided by the whole, times a hundred, is the percentage of A. The intuition is a recipe. If a cake takes 2 cups of flour and 1 of sugar, then flour is two cups out of three, whatever size of cake you bake. A formula is a recipe for a substance, and the atomic weights turn its counts into weights.



A Formula Is a Recipe

Mendeleev's own example is common salt, NaCl, with sodium Na = 23 and chlorine Cl = 35.5, and one of each, so n and m are both 1. The whole unit weighs $23 + 35.5 = 58.5$. Sodium is $23 \cdot 100 / 58.5$, which is

about 39.3 per cent. Chlorine is $35.5 \cdot 100/58.5$, about 60.7 per cent. And the two add to a hundred, as they must.



$$23 + 35.5 = 58.5$$



Na 39.3 %

Cl 60.7 %



1000 G



393 G

607 G

$$393 + 607 = 1000$$

Salt: 39.3 and 60.7 Per Cent

This is where the formula pays off, Mendeleev says: give me the real weight of a compound, and the formula tells me the real weight of each simple body in it. Take a kilogram of salt, 1000 grams. Sodium is 39.3 per cent of it, so about 393 grams; chlorine is the other 607 grams. The packet of salt in your kitchen, if it weighs a kilogram, holds about 393 grams of a soft metal that would catch fire in water, and about 607 grams of a poisonous green gas, locked together into something you sprinkle on food. That last thought is Mendeleev's point about simple bodies made vivid: the sodium and the chlorine are in the salt, yet neither the metal nor the gas is there as such.

Try it yourself

Take a teaspoon of salt and weigh it on a kitchen scale; suppose it weighs 6 grams. Using the share of 39.3 per cent, work out how much of it is sodium: about 2.4 grams. Now read the nutrition label on a packet of salty food, where sodium is often listed separately from salt. Multiply the sodium figure by $100/39.3$, about 2.5, and you get the salt it corresponds to: the label is using Mendeleev's formula.

Remember

Breaking substances into their parts ends at simple bodies, which can be neither decomposed nor built from anything else; everything else is a compound. Simple bodies do not turn into one another, so the amount of each stays the same through every chemical change. Each simple body is written with letters from its Latin name, and each letter also stands for a fixed weight, the weight of its atom. For a compound A_nB_m , the percentage of A is $na \cdot 100 / (na + mb)$, like reading the share of flour from a recipe. Common salt, NaCl, with Na = 23 and Cl = 35.5, is 39.3 per cent sodium and 60.7 per cent chlorine.

Questions

1. Chalk can be broken into lime and carbonic acid gas and made again from them. Why are lime and the gas still not simple

bodies?

- a. Because they can themselves be broken down: the gas into carbon and oxygen, lime into calcium and oxygen
 - b. Because they are found only in chalk
 - c. Because any substance made in a fire is a compound
 - d. Because they cannot combine with anything
2. Why does the amount of each simple body stay the same through every chemical change?
- a. Because simple bodies are too stable to react
 - b. Because a simple body cannot be decomposed or turned into another, and matter is never lost or created
 - c. Because the balance weighs each simple body separately
 - d. Because formulas are always written with letters
3. A compound has the formula A_nB_m . If you double both n and m , what happens to the percentage of A?
- a. It doubles
 - b. It halves
 - c. It stays the same, because both the part of A and the whole are doubled
 - d. It becomes a hundred per cent
4. What can you work out from a formula once you know the real weight of a compound?
- a. Its temperature of decomposition
 - b. Its colour and taste
 - c. The number of simple bodies known
 - d. The real weight of each simple body in it

Answers

- 1. a)** Carbonic acid gas is carbon combined with oxygen, and lime is the oxide of the metal calcium, so both are compounds.
- 2. b)** A simple body cannot be decomposed, and matter is never lost or created; therefore the amount of each simple body stays the same.
- 3. c)** The share of A is the part of A divided by the whole, times a hundred; doubling everything leaves the share unchanged, just as with a recipe.
- 4. d)** Give the real weight of a compound, and the formula tells you the real weight of each simple body in it.

Worked examples

Percentages in common salt Common salt is NaCl, with Na = 23 and Cl = 35.5. Find the percentage of sodium and of chlorine, and the weight of sodium in 200 grams of salt.

Here $n = m = 1$, so one unit of salt weighs $na + mb = 23 + 35.5 = 58.5$.

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

Chlorine: $35.5 \times 100 / 58.5$, about 60.7 per cent; the two add up to 100.

In 200 grams of salt, sodium is 39.3 per cent of 200, about 78.6 grams.

Answer: 39.3 per cent sodium, 60.7 per cent chlorine; about 78.6 grams of sodium in 200 grams of salt

Practice

- 1.** How many grams of chlorine are there in 50 grams of common salt, NaCl, with Na = 23 and Cl = 35.5?

Hint: Find chlorine's share $35.5/58.5$ first.

Answer: About 30.3 grams. Chlorine is $35.5/58.5$, about 60.7 per cent, of the salt, and 60.7 per cent of 50 grams is about 30.3 grams.

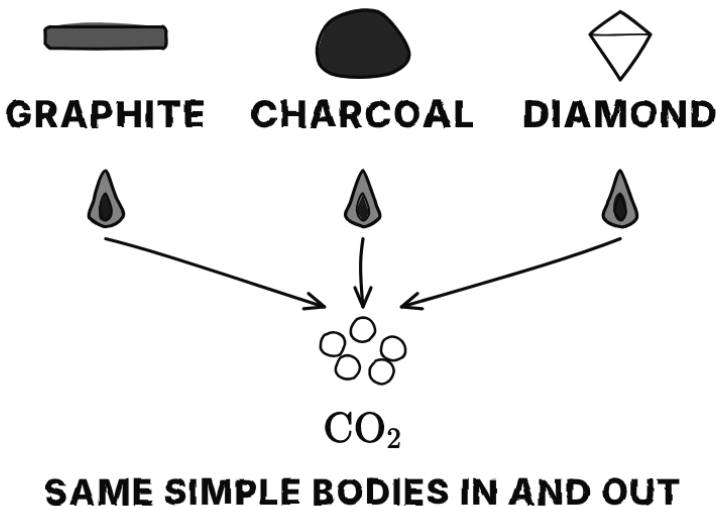
2. A compound AB_2 contains one proportion of A with weight $a = 12$ and two proportions of B with weight $b = 16$. What percentage of it is A?

Hint: Here $n = 1$ and $m = 2$; put them into $na \cdot 100 / (na + mb)$.

Answer: About 27.3 per cent. The whole is $na + mb = 12 + 32 = 44$, so A is $12 \times 100 / 44$, about 27.3 per cent, and B is the remaining 72.7 per cent.

Elements, Not Ingredients

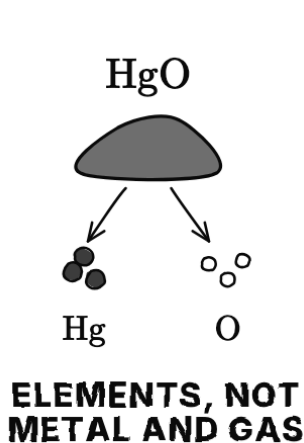
A pencil lead, a lump of barbecue charcoal and a diamond ring look about as different as three things can. One is grey and slippery, one black and crumbly, one clear and harder than anything else. Yet burn any of them in oxygen, and each gives the same gas, carbonic acid gas, and nothing else. The charcoal in a garden grill and the diamond in a jeweller's window are, to a chemist, the same element in two different coats. How can three different simple bodies be one and the same thing? Answering that is the main business of this part.



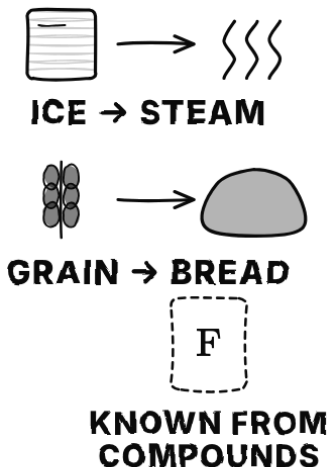
Three Bodies, One Gas

First, Mendeleev draws the consequence of the last part. Since simple bodies never turn into one another, a substance can be turned only into substances that contain the same simple bodies. From salt you can get sodium and chlorine compounds, but never an ounce of iron; that is the limit on chemical change that the alchemists never found. Yet even within this limit the number of possible compounds is endless. Only a small share had been studied, and anyone setting to work could easily make a substance nobody had made before; many such substances, he adds, are predicted by science before anyone makes them. So the aim of chemistry is not to list compounds one by one. It is to grasp the regularity hidden in their multitude: the laws that govern how they form and what properties they have. In practice that means four tasks: finding the properties of a compound from the kind and amount of its simple bodies; studying the simple bodies themselves; finding which compounds each simple body can form, and with what properties; and understanding the bond that holds simple bodies together inside compounds.

Now a subtle point, and Mendeleev takes care over it. When we say that red mercury oxide contains oxygen, we do not mean that a bubble of oxygen gas is sitting inside the red powder. We mean something about what the powder can do: that mercury and oxygen can be got out of it, and that it can hand them over to other bodies. His summary is worth keeping: the composition of a compound is the expression of the transformations it is capable of.



SUBSTANCE, NOT THE THING

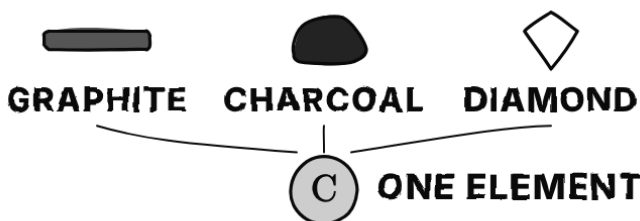


Elements, Not Ingredients

That is why he separates two ideas that everyday language mixes up. A simple body is a separate substance you can hold: shiny liquid mercury, or oxygen gas in a jar. An element is the material part that the simple body and all its compounds share. Red mercury oxide contains not two simple bodies, a metal and a gas, but two elements, mercury and oxygen. Mendeleev gives two comparisons. Steam contains the substance of ice, but not ice itself; bread contains the substance of grain, but not the grain.

Three facts show that the difference is real. The first is fluorine. For a long time nobody had ever obtained fluorine on its own, yet chemists had to count it as an element, because its compounds were known and behaved differently from all similar compounds. An element can be

known from its compounds before its simple body is ever seen. The second is that compounds can themselves combine into still more complex compounds, and then be got back out of them by the same means that free simple bodies from theirs, so being extracted from a compound does not by itself make something simple. The third is the pencil, the charcoal and the diamond. They are three different simple bodies, which Mendeleev calls modifications, but their element is one, carbon. And carbonic acid gas contains carbon too, though it holds no charcoal, no graphite and no diamond.



$\text{CO}_2 : \text{C} = 12, \text{O} = 16$

$$12 + 2 \times 16 = 44$$



C 27.3 %

O 72.7 %

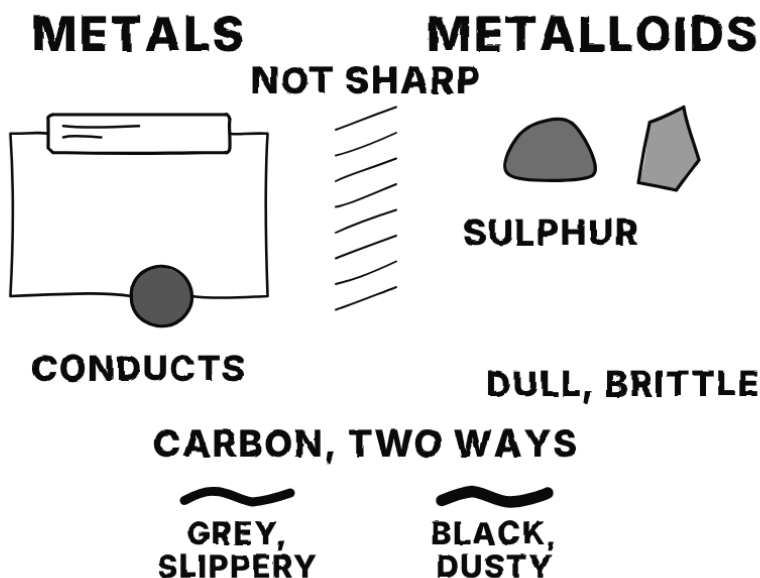
12 G CARBON → 44 G GAS

Carbon Is 27.3 Per Cent

Here the formula from the last part lets us see this as a calculation. In today's notation carbonic acid gas is CO_2 , with carbon $\text{C} = 12$ and oxygen $\text{O} = 16$. One unit weighs $12 + 2 \times 16 = 44$. So carbon is 12 ·

100/44, about 27.3 per cent of the gas. In words: whether you burn 12 grams of graphite, of charcoal or of diamond, you get 44 grams of the same gas, and 12 grams of it is carbon. The simple bodies differ; the element, and its weight in the compound, do not.

Mendeleev then notes a looser grouping. Many simple bodies, though not all, have a metallic lustre, are opaque, can be hammered into shape, and conduct heat and electricity well; these are the metals, and their mixtures with each other are alloys. The rest are called metalloids. In sharp cases the two kinds are easy to tell apart, but in many cases the line is blurred, so this division cannot be an exact basis for classifying the simple bodies.



Try it yourself

Hold a short piece of pencil lead with tweezers in the flame of a gas burner or a candle. It glows but burns only very slowly, and leaves almost nothing behind. Rub a little of the same lead on paper and it leaves a grey, slippery trace, quite unlike charcoal, which leaves a black, dusty one. The two look and behave differently, yet both are carbon: given enough heat and oxygen, both disappear into the same invisible gas.

Finally Mendeleev explains why he gives a list of the simple bodies right at the start of his book. The idea of elements and simple bodies is the foundation of chemistry, and the list shows what was known at that moment. About eighty simple bodies were recognised, but about six of them were so rare and had been obtained in such tiny amounts that knowledge of them was thin. The common bodies of nature are made of only a few simple bodies, and those are known best, simply because so many people have been able to experiment on them. Which are they? That list is where the next part begins.

Remember

A substance can only be turned into substances containing the same simple bodies, yet the possible compounds are endless, so chemistry looks for the laws behind them. The composition of a compound expresses what it can be turned into, not ready-made pieces sitting inside it. A simple body is a separate substance; an element is the material part shared by that simple body and all its compounds. Charcoal, graphite and diamond are three simple bodies but one element, carbon, which is about 27.3 per cent of carbonic acid gas. Metals and metalloids are a useful but blurred division, and of about eighty simple bodies the common ones are known best.

Questions

1. Why can no amount of chemical work turn common salt into iron?
 - a. Because a substance can be turned only into substances containing the same simple bodies
 - b. Because salt dissolves in water and iron does not
 - c. Because iron is heavier than salt
 - d. Because salt is a simple body
2. What do we really mean when we say red mercury oxide contains oxygen?
 - a. That oxygen gas is trapped inside the powder

- b. That mercury and oxygen can be obtained from it and it can hand them to other bodies
 - c. That it smells of oxygen when warmed
 - d. That it weighs the same as oxygen
3. How could fluorine be counted as an element before anyone had obtained it on its own?
- a. Because it was predicted by the four-element theory
 - b. Because it is found free in the air
 - c. Because its compounds were known and differed from all similar compounds
4. Why can the division into metals and metalloids not serve as an exact classification of simple bodies?
- a. Because metals cannot be obtained pure
 - b. Because metalloids conduct electricity better than metals
 - c. Because all simple bodies are really metals
 - d. Because in many cases the line between the two kinds is blurred

Answers

1. **a)** Since simple bodies never turn into one another, a substance can be turned only into substances that contain the same simple bodies.
2. **b)** We mean something about what the powder can do; the composition of a compound is the expression of the transformations it is capable of.
3. **c)** An element can be known from its compounds before its simple body is ever seen.

4. d) In sharp cases the two kinds are easy to tell apart, but in many cases the line is blurred.

Practice

1. Explain in your own words the difference between a simple body and an element, using red mercury oxide as the example.

Hint: Ask what you could put in a jar, and what the oxide and its products have in common.

Answer: A simple body is a separate substance, like liquid mercury or oxygen gas in a jar. An element is the material part shared by that simple body and all its compounds. Red mercury oxide contains not the metal and the gas, but the elements mercury and oxygen, as steam contains the substance of ice but not ice itself.

2. Charcoal, graphite and diamond are different simple bodies. Explain why chemists still say they have one element, and what carbonic acid gas has to do with it.

Hint: Think about what all three have in common with each other and with the gas.

Answer: They are different modifications, but they share one element, carbon, which is not subject to change. The same carbon is contained in carbonic acid gas, yet the gas holds no charcoal, graphite or diamond: the element is there, not any of its simple bodies.

3. If simple bodies never change into one another, why is the number of possible compounds still said to be endless, and what then is chemistry's aim?

Hint: Think of how many ways a small number of simple bodies can combine.

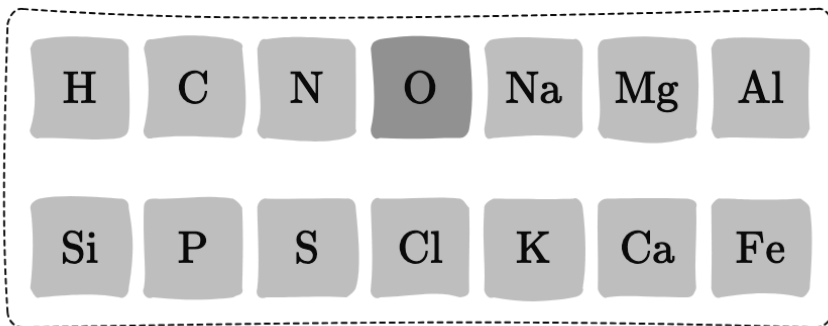
Answer: Even a limited set of simple bodies can combine in endlessly many ways and proportions, so new compounds can always be made, and

many are predicted before they are made. Chemistry's aim is therefore not to list them but to find the regularities, the laws governing how compounds form and what properties they have.

A Roll Call of the Elements, and the Force That Binds Them

Look around a kitchen and try to name the simple bodies hiding in it. The water in the kettle is hydrogen and oxygen. The salt is sodium and chlorine. The steel of the knives is mostly iron, the sugar is carbon, hydrogen and oxygen, and the glass of the windows is mostly silicon and oxygen. A single kitchen, in other words, already contains most of the simple bodies that matter in everyday life. Mendeleev makes the same point with a list, and this part walks through it, then turns to the force that holds the elements together.

THE MOST WIDESPREAD FOURTEEN



He sorts the simple bodies into groups. First come the fourteen most widespread in nature, each written with its symbol and where it is found. Hydrogen, H, is in water and in living things. Carbon, C, is in living things, coal and limestone. Nitrogen, N, is in the air and in living things. Oxygen, O, is in the air, in water and in the earth, and its mass is the greatest of all. Then sodium, Na, in common salt and many stones; magnesium, Mg, in sea water and stones; aluminium, Al, in stones and clay; and silicon, Si, in sand, clay and stones. Phosphorus, P, is in bones, plant ash and soil; sulphur, S, in pyrites, gypsum and sea water; chlorine, Cl, in salt and sea water. And finally potassium, K, in stones, plant ash and saltpetre; calcium, Ca, in limestone, gypsum and living things; and iron, Fe, in soil, iron ores and living things.

Notice the symbols that do not match the English names. Sodium is Na from the Latin natrium, potassium is K from kalium, and iron is Fe from ferrum: the rule from the last parts, one or two first letters of the Latin name. Notice too how few these fourteen are. Almost everything you can touch, from rocks to your own body, is built from this short list.

Next comes a longer group: simple bodies that are not common in nature, but are used in daily life or industry. Here Mendeleev gives formulas, and they are worth reading slowly, because each formula is a short recipe. Lithium, Li, appears in medicine as Li_2CO_3 : two lithiums, one carbon and three oxygens. Fluorine, F, appears in fluor spar, CaF_2 : one calcium to two fluorines. Barium, Ba, appears in heavy spar, BaSO_4 , a very dense white mineral. Arsenic, As, appears as white arsenic, the poison As_2O_3 . Boron gives borax and boric acid; chromium and manganese give strong colours and strong oxidisers, among them "chameleon", the purple permanganate that changes

colour as it reacts. Cobalt colours glass blue, nickel is plated onto other metals, zinc goes into sheets, batteries and brass, and copper is the familiar red metal. Bromine is a brown liquid that evaporates easily; strontium gives the red of Bengal fires; cadmium gives a yellow paint, CdS; antimony goes into the alloy of printing type; iodine is used in medicine and photography. Silver, tin, platinum, gold, mercury and lead need no introduction, and bismuth is used in medicine and in alloys that melt at low heat.

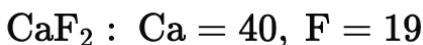
EACH FORMULA IS A RECIPE



Formulas as Recipes

Let us read one of these formulas with numbers, the way the last parts taught. Take fluorspar, CaF_2 , with calcium $\text{Ca} = 40$ and fluorine $\text{F} = 19$. One unit holds one calcium and two fluorines, so it weighs $40 + 2 \times 19 = 78$. Calcium is $40 \cdot 100/78$, about 51.3 per cent; fluorine is the

remaining 48.7 per cent. In words: a 100-gram crystal of fluorspar holds about 51 grams of calcium and 49 of fluorine, though you would never see either as such. A tube of fluoride toothpaste traces back to the same element; fluorine in it comes as a compound, never as the free yellowish gas.



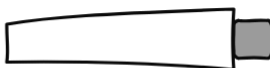
$$40 + 2 \times 19 = 78$$



Ca 51.3 %

F 48.7 %

$$100 \text{ G} \rightarrow 51 \text{ G} + 49 \text{ G}$$

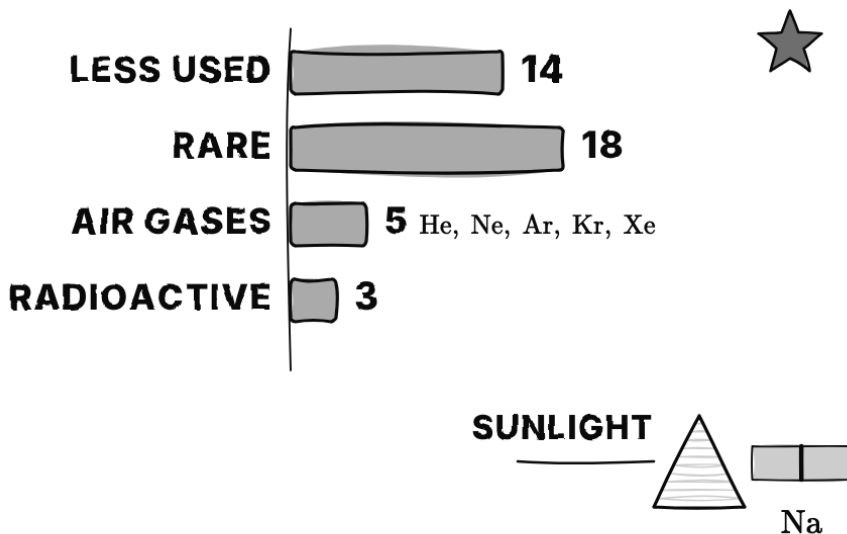


FLUORIDE: A COMPOUND

Fluorspar: 51.3 Per Cent Calcium

Then come two groups of rarer elements. Fourteen are well known and turn up fairly often in nature in small amounts, but have few uses: among them titanium, tungsten, uranium and thorium.

Eighteen more are rarer still and had no practical use in Mendeleev's day, though their compounds had been studied with some care: among them gallium, germanium and scandium.



The Rarer Groups

Then a special group: the gases discovered by Ramsay, present in small amounts in the air, and unlike every other element in one striking way. Nobody had yet managed to make a single compound of them with any other element. They are helium, neon, argon, krypton and xenon. The neon in an old shop sign and the argon inside many light bulbs belong to this group, chosen precisely because they react with almost nothing. After them, Mendeleev mentions some grounds for counting the metals actinium, polonium and radium, discovered by Madame Curie, which occur in tiny amounts in compounds of uranium and thorium and are called radioactive. That brings his count to seventy-seven, with a few more, such as gadolinium and terbium, so rare that their properties were barely known and some were not yet certain to be separate elements at all.

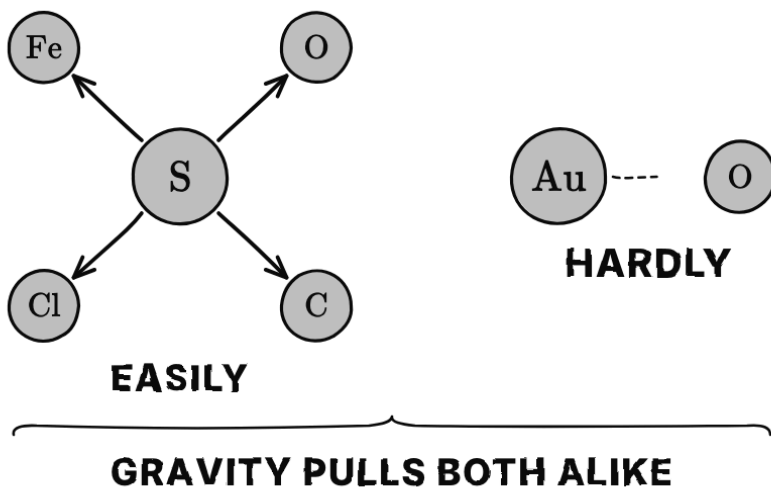
Two remarks close the survey. The first is astonishing even now. By studying the light of distant stars and of the sun, chemists had proved beyond doubt that hydrogen, sodium, magnesium, iron and other common elements of the earth are there too. So the simple bodies we know on earth are not a local accident; the same matter is spread through the universe. The second is a confession: why some elements are so plentiful and others so rare, nobody yet knew.

Try it yourself

Hold a pinch of table salt in the blue flame of a gas burner and watch the flame flash bright yellow. That yellow is the light of sodium. Split the sun's light with a prism, and at exactly that shade of yellow there is a dark line, the mark of sodium in the sun. That match of light is how chemists proved that sodium exists on the sun without ever going there.

Now Mendeleev turns from the list to what makes each element what it is. Every element has its own readiness to combine with others, to form compounds that are more or less stable, and to go on into still more complex ones; that readiness is its basic character. Sulphur combines easily with metals, with oxygen, with chlorine and with carbon. Silver and gold combine reluctantly, and many of their compounds are fragile and fall apart when heated. The cause that drives substances to change is the same cause that then holds the elements together and gives a compound its stability. Chemists call it affinity, or chemical affinity.

AFFINITY

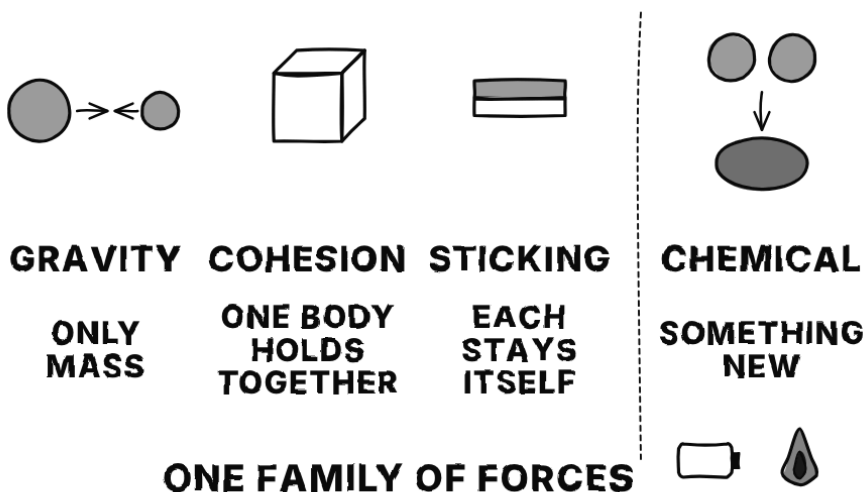


Some Join Easily, Some Hardly

What is affinity like? It pulls, and only pulls, so in the late eighteenth and early nineteenth centuries Bergman and Berthollet guessed that it might simply be gravity, acting at tiny distances instead of large ones. Mendeleev answers no. Gravity depends only on masses and distances, never on what the substance is; affinity depends very strongly on what the substances are. A gram of sulphur and a gram of gold attract a third body equally by gravity, yet they could not be more different in their eagerness to combine.

Nor is affinity the same as cohesion, the force that holds one substance together, gives a solid its hardness, crystal shape and springiness, and gives a liquid its drops and its rise in thin tubes. Cohesion acts between like particles, affinity between unlike ones,

though both act only at contact and have much in common. And affinity is not the sticking of unlike things either: two polished plates that cling together, water wetting glass, a gas condensing on a surface. In sticking, nothing new is formed; in a chemical change one substance enters the other and a new one appears. Still, Mendeleev admits, these sticking forces are a kind of bridge between the mechanical and the chemical, because they too act only at full contact.



Not Gravity, Cohesion or Sticking

For much of the nineteenth century, chemists identified chemical forces with electrical ones. There is a close link: reactions produce electricity, and an electric current can decompose compounds. But heat has exactly the same kind of link: reactions produce heat, and heat can decompose compounds. Such links show only that the forces

of nature are one family, able to turn into each other, not that chemical force is electricity; and the electrical theory failed when it was tested.

So what is left? Heat is the best understood of all the hidden motions of matter, because it has been reduced to the simple ideas of mechanics, energy, equilibrium and motion, which since Newton can be handled with exact mathematics. It is natural, then, to try to connect chemistry with heat, without claiming that chemical changes are nothing but heat. Mendeleev draws a comparison with astronomy. Nobody knows what gravity really is, yet by applying mechanics astronomers predict the planets in great detail; in the same way, without knowing what affinity really is, chemists may hope to make great progress through the mechanical theory of heat. This field is still unfinished, and it is called theoretical or physical chemistry, though Mendeleev's own preferred name is chemical mechanics. And because it assumes you already know the substances, how they change and what accompanies their changes, it can only come after the basic ideas and the substances themselves, which are what his book sets out to teach.

Remember

Fourteen simple bodies, among them hydrogen, carbon, nitrogen, oxygen, silicon, calcium and iron, make up almost all the common matter of nature, with oxygen the most plentiful. A formula such as CaF_2 is a recipe that, with the atomic weights, gives the share of each element, here about 51 per cent calcium. Rarer groups follow, including Ramsay's gases, which form no compounds at all, and the radioactive metals; and the light of stars shows that the same elements exist across the universe. Each element has its own readiness to combine, and the force behind it, chemical affinity, depends on what the substances are, unlike gravity, cohesion or electricity. The nature of affinity is unknown, so chemical mechanics hopes to make progress through the mechanical theory of heat, after the substances themselves are known.

Questions

1. Why is potassium written K and iron written Fe?
 - a. Because symbols come from the first letters of the Latin names, kalium and ferrum
 - b. Because the English names were already taken by other elements
 - c. Because those symbols were chosen at random
 - d. Because they are abbreviations of German names

2. What sets the gases discovered by Ramsay apart from all other elements?
 - a. They are the heaviest elements known
 - b. Nobody had yet made a single compound of them with any other element
 - c. They are found only on the sun
 - d. They are radioactive
3. Why can chemical affinity not simply be gravity acting at small distances?
 - a. Because gravity pushes as well as pulls
 - b. Because affinity works only in liquids
 - c. Because gravity depends only on mass and distance, while affinity depends strongly on what the substances are
4. Why does Mendeleev say that chemistry's link with electricity does not prove chemical forces are electrical?
 - a. Because electricity has no effect on compounds
 - b. Because reactions never produce electricity
 - c. Because electricity was not yet understood at all
 - d. Because heat has exactly the same kind of link, which shows only that the forces of nature turn into one another

Answers

1. a) Each simple body gets one or two first letters of its Latin name: potassium is K from kalium and iron Fe from ferrum.
2. b) Nobody had yet managed to make a single compound of helium, neon, argon, krypton or xenon with any other element.

3. **c)** Gravity depends only on masses and distances, never on what the substance is; affinity depends very strongly on what the substances are.
4. **d)** Heat too is produced by reactions and can decompose compounds; such links show only that the forces of nature are one family, able to turn into each other.

Practice

1. Sulphur combines easily with metals, oxygen, chlorine and carbon; silver and gold combine reluctantly and their compounds fall apart when heated. Explain what this tells you about the character of an element, and what name is given to the cause.

Hint: Think of what the cause does both before and after a compound is formed.

Answer: Each element has its own readiness to combine and to form more or less stable compounds, and that is its basic character. The cause that drives substances to change is the same that holds the elements together in the compound and gives it stability; it is called chemical affinity.

2. Explain how affinity differs from cohesion and from the sticking together of two polished plates.

Hint: Ask between which particles each force acts, and whether anything new is formed.

Answer: Cohesion acts between particles of the same substance, holding it together; affinity acts between unlike substances. Sticking also acts between unlike bodies, but nothing new is formed; in a chemical change one substance enters the other and a new substance appears. All of them act only at contact.

3. Mendeleev compares chemical mechanics with astronomy. Explain the comparison and why chemical mechanics has to come after

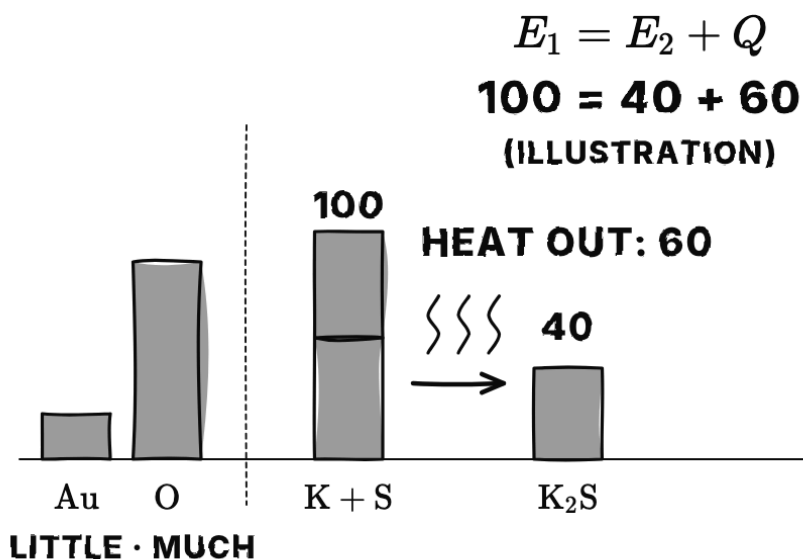
learning the substances themselves.

Hint: What is unknown about gravity, and what did astronomers still achieve?

Answer: Nobody knows what gravity really is, yet mechanics lets astronomers predict the heavens in detail; likewise, without knowing what affinity is, chemists hope to progress through the mechanical theory of heat. But chemical mechanics assumes that the substances, their transformations and what accompanies them are already known, so it can only follow the study of the basic ideas and substances.

Stored Energy, Fixed Recipes and Roads That Run Both Ways

Touch a lump of potassium to a flame and it burns fiercely; do the same with sulphur, and it burns with a blue flame. Now heat the two together until they combine, and try to light what you get. It will not burn in air the way either of them did. Something has gone out of them, and Mendeleev says what: energy, released as heat at the moment they combined.



Energy Out as Heat

His reasoning runs like this. Chemical changes come from forces inside substances; chemical events are always motions of tiny material parts; and physics has shown that energy is conserved, only changing its form. So every substance, and every element in particular, must hold a store of chemical energy, an invisible motion that drives it into reactions. When a reaction gives off heat, part of that chemical energy has turned into heat. When a reaction takes in heat, the heat is partly hidden away as chemical energy. A battery is a store of this kind: chemical energy packed in at the factory, released as electricity when the circuit closes.

Let us write the bookkeeping as a formula, in the spirit of the law of conservation. Call the chemical energy of the starting substances E_1 , that of the products E_2 , and the heat given out Q . Then $E_1 = E_2 + Q$. In words: the energy before equals the energy after plus whatever left as heat. The intuition is a bank account: if you spend from it, the balance drops by exactly what you spent. As a calculation, suppose the potassium and sulphur held 100 units of chemical energy, and combining gave off 60 units of heat; the compound keeps $100 - 60 = 40$ units, too few to burn as the elements did. Those numbers are only for illustration; the book gives none, but the logic is the book's.

After several combinations, each giving off heat, a substance may be left with so little energy that it hardly reacts at all. Yet even then it is not finished: such a sluggish compound can combine with an energetic element or compound and make something more complex that is lively again. Some simple bodies hold little energy, such as gold, platinum and nitrogen; others hold a great deal, such as potassium, chlorine and oxygen. And unlike bodies, when they combine, often give compounds with less energy, just as potassium and sulphur did. In short, Mendeleev says, just as a substance takes in

or gives out heat when it melts or boils, so every combination and decomposition changes its store of chemical energy and gives out or takes in heat.

To study how reactions run, the field he calls chemical mechanics, Mendeleev names five things that matter most. First, stoichiometry: the study of how much of each substance reacts, by weight and by volume. Second, the different kinds of chemical interaction; third, how properties change when composition changes; fourth, what accompanies a reaction, such as heat; and fifth, the conditions under which reactions happen. Of these, stoichiometry was the most complete. Its laws, found by Dalton, by Avogadro and Gerhardt and by others, run so deep that Mendeleev calls his whole age the epoch of applying them, and he says that everything in his book is arranged under them.

STOICHIOMETRY

DALTON · AVOGADRO · GERHARDT

DEFINITE



Hg 200

$$16 \cdot 100/216 \approx 7.4 \%$$

108 G → 8 G OXYGEN

INDEFINITE



ANY SHARE

Fixed and Sliding Recipes

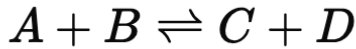
Stoichiometry brought a new division of compounds into definite and indefinite. At the start of the nineteenth century Berthollet made no such distinction. Then Proust showed that very many compounds contain their parts in an exact proportion by weight that never changes, whatever the conditions. Mendeleev's example is red mercury oxide: 16 parts of oxygen to every 200 parts of mercury, written HgO. Let us use that proportion aloud. The whole unit weighs $200 + 16 = 216$ parts, so oxygen is $16 \cdot 100/216$, about 7.4 per cent. In words: any sample of red mercury oxide, from any source, is about 7.4 per cent oxygen by weight; 108 grams of it, for example, hold $108 \times 16/216 = 8$ grams of oxygen and 100 of mercury.

An alloy of copper and silver is different. You can add any amount of either metal and still get a uniform whole, whose properties are a blend of the parts. A solution of sugar in water is the same: you can make it weaker or stronger as you please. These are indefinite compounds. The brass of a door handle and the sweet tea in a cup are both indefinite compounds in this sense; the recipe can slide.

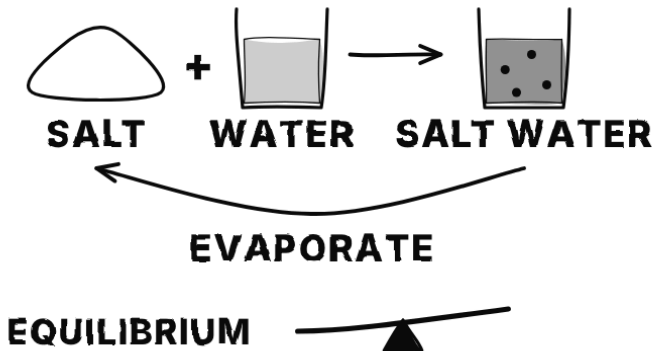
Mendeleev stresses that alloys and solutions matter just as much in nature, in labs and in factories, but because the laws of stoichiometry were worked out on definite compounds, much less was known about the indefinite ones, and only lately had chemists turned to them.

Next he separates reversible reactions from irreversible ones. A reaction is reversible if, at the same temperature, its products can turn back into the starting substances. Salt dissolves in water at room temperature, and at the same temperature the solution gives the salt back as the water evaporates. Carbon disulphide forms from sulphur and charcoal at a temperature at which it can also split back into them. Red-hot iron takes oxygen from water and sets hydrogen free, making iron oxide; yet at that same temperature hydrogen turns the iron oxide back into iron and water.

REVERSIBLE



MORE B ↑

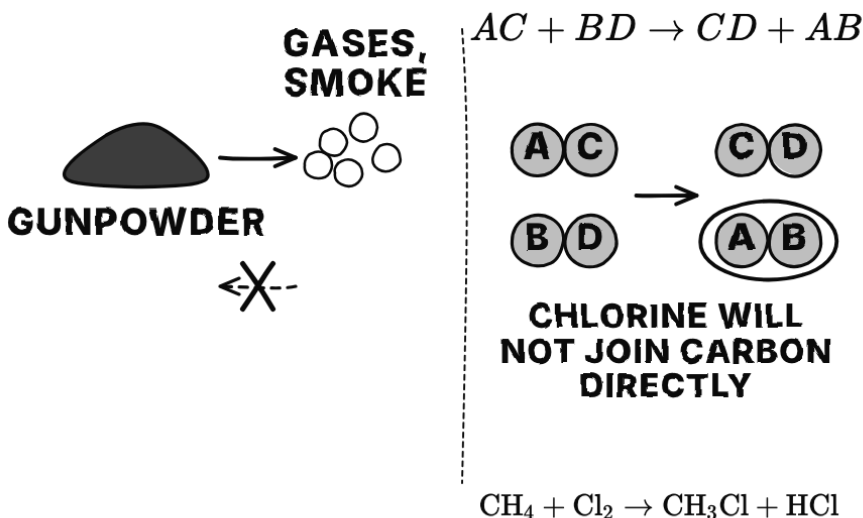


Roads That Run Both Ways

Write it with letters: $A + B \rightleftharpoons C + D$, where the double arrow means the road runs both ways. Start from A and B, or start from the matching amounts of C and D, and either way you end with all four side by side. That state is called chemical equilibrium. The intuition is two rooms joined by an open door, with people drifting both ways: after a while the numbers in each room stop changing, though people still cross. Add more of one substance, and the balance shifts to a new position; so reversible reactions let chemists study how the amount of a substance affects the course of a reaction.

Irreversible reactions are common among very complex substances and mixtures. Many substances of plants and animals fall apart when heated, but their pieces never rebuild them at any temperature.

Gunpowder, a mixture of saltpetre, sulphur and charcoal, burns to gases and smoke, and those never turn back into gunpowder. To make such things again you need a roundabout way.



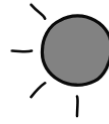
One Way, and a Detour

That roundabout way is Mendeleev's last and subtlest point: a failure to combine directly does not mean two elements cannot form a compound. Suppose A never joins B directly. Put A with C, and B with D, and choose C and D so that they have a strong affinity for each other. Then $AC + BD \rightarrow CD + AB$. In words: C and D rush together, and A and B, left suddenly free at the same spot, join each other. The idea is that substances are especially ready to combine at the moment they are set free, "in the nascent state", in *statu nascendi* as the Latin has it.

His example is chlorine and carbon. Chlorine does not react directly with charcoal, graphite or diamond, yet many compounds of chlorine and carbon exist, some of them very stable. They are made by letting chlorine act on hydrocarbons, compounds of carbon and hydrogen. In today's notation the simplest case is $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$. In words: chlorine pulls hydrogen away, and the carbon, freed at that instant, takes up chlorine in its place, so the chlorine ends up joined to both hydrogen and carbon.

Try it yourself

Dissolve a spoonful of salt in a saucer of water and leave the saucer on a sunny windowsill for a few days. As the water evaporates, salt crystals appear at the edges and then across the bottom. Add water again, and they dissolve; let it dry, and they return. At the same room temperature the change runs both ways, which is exactly what Mendeleev means by a reversible reaction.



DRY $\rightleftharpoons$ WET

A FEW DAYS



CRYSTALS

SAME TEMPERATURE, BOTH WAYS

Salt That Comes and Goes

Remember

Every substance holds a store of chemical energy; heat given out in a reaction is energy that has left that store, and heat taken in is partly stored. Stoichiometry, the study of how much reacts, was the most complete part of chemistry, and it divides compounds into definite and indefinite. A definite compound has a fixed proportion, like red mercury oxide with 16 parts of oxygen to 200 of mercury, about 7.4 per cent oxygen; alloys and solutions can vary. In a reversible reaction the products can give back the starting substances at the same temperature, and all four end in equilibrium; in an irreversible one they cannot. Elements that never combine directly can still be joined by a roundabout way, meeting at the moment they are set free, as carbon and chlorine do.

Questions

1. Potassium and sulphur each burn readily, but their compound does not burn in air the same way. What is the explanation?
 - a. Part of their chemical energy left as heat when they combined, so the compound has less
 - b. The compound contains no potassium or sulphur
 - c. Combination doubles the energy, making the compound too stable
 - d. The compound cannot be heated

2. What did Proust show that Berthollet had not distinguished?
- That all compounds can have any proportions
 - That many compounds hold their parts in an exact proportion by weight that never changes
 - That alloys are simple bodies
 - That heat has no effect on compounds
3. In a reversible reaction $A + B \rightleftharpoons C + D$, what is found at the end if you start from C and D alone?
- Only C and D, unchanged
 - Only A and B, completely converted
 - All four, side by side, in chemical equilibrium
 - A new substance formed in the nascent state
4. Chlorine never reacts directly with charcoal, yet chlorine-carbon compounds exist. How does that fit Mendeleev's idea?
- Chlorine reacts with carbon only in light
 - The compounds are made by heating chlorine with diamond
 - The compounds are really mixtures, not compounds
 - Chlorine acting on hydrocarbons frees carbon at the moment it can take up chlorine, in the nascent state

Answers

1. **a)** Something has gone out of them: energy, released as heat at the moment they combined.
2. **b)** Proust showed that very many compounds contain their parts in an exact proportion by weight that never changes, whatever the conditions.

3. **c)** Start from A and B, or from the matching amounts of C and D, and either way you end with all four side by side: chemical equilibrium.

4. **d)** Chlorine pulls hydrogen away, and the carbon, freed at that instant, takes up chlorine in its place.

Worked examples

Oxygen in red mercury oxide Red mercury oxide contains 16 parts of oxygen to 200 parts of mercury, a fixed proportion. What percentage of it is oxygen, and how many grams of oxygen are there in 108 grams of it?

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

The percentage of oxygen is $16 \times 100 / 216$, about 7.4 per cent.

In 108 grams there are $108 \times 16 / 216$ grams of oxygen.

$108/216$ is one half, so this is $16/2 = 8$ grams, and the remaining 100 grams are mercury.

Answer: About 7.4 per cent; 8 grams of oxygen in 108 grams

Practice

1. How much red mercury oxide can be made from 50 grams of mercury, if the oxide always holds 16 parts of oxygen to 200 of mercury?

Hint: Find how much oxygen goes with 50 grams of mercury, then add.

Answer: 54 grams. 50 is a quarter of 200, so it takes a quarter of 16, that is 4 grams of oxygen, and $50 + 4 = 54$ grams of oxide.

2. A mixture of copper and silver can be made with any proportions, while red mercury oxide cannot. Explain which is a definite

compound and which an indefinite one, and why stoichiometry knew more about the first kind.

Hint: Ask whether the proportion by weight can change.

Answer: Red mercury oxide is definite: its proportion by weight is fixed. The copper-silver alloy is indefinite: any amount of either metal can be added and the whole stays uniform. The laws of stoichiometry were worked out chiefly on definite compounds, so knowledge of indefinite ones, alloys and solutions, was less complete.

3. Explain why burning gunpowder is called irreversible, and why salt dissolving in water is called reversible.

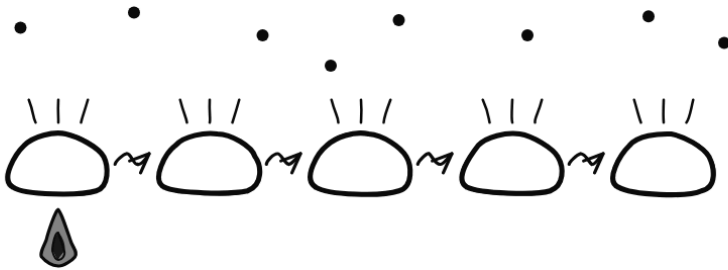
Hint: Can the products give back the starting substances at the same temperature?

Answer: The gases and smoke of gunpowder never turn back into saltpetre, sulphur and charcoal at any temperature, so that reaction is irreversible. Salt solution gives back salt as the water evaporates at the same temperature, so dissolving is reversible.

Heat, Work and the Temperature Window

Hold a lump of charcoal in the air of a cool room. It is surrounded by oxygen, the very gas it burns in, and yet nothing happens; it can lie there for years. Now touch one corner with a flame until it glows red. The glowing spot catches, gives off heat, makes the spot beside it glow, and soon the whole lump is burning on its own. A barbecue starter works on exactly this: you only need to make one corner of the charcoal red-hot, and the rest follows. Why should oxygen and charcoal, perfectly willing to combine, wait for heat before they do?

OXYGEN OF THE AIR

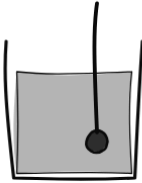


RED-HOT THE HEAT SPREADS

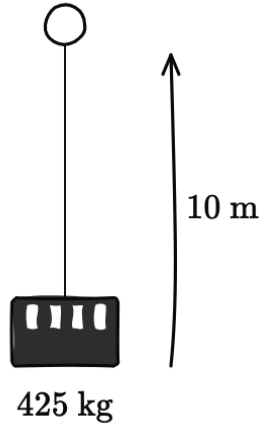
Mendeleev begins with a wider principle. A chemical reaction does not only produce motion, heat, light, electrical tension and current; each of these, in turn, can change the course of a reaction. The influence runs both ways, and he explains why: all the phenomena of nature are different kinds of motion, visible and invisible, the invisible ones being the motions of molecules. Physics had shown that sound and then light are vibrations, and that heat is bound to mechanical work.

That last link has an exact number, and it is the formula of this part. Mendeleev writes it in the units of his day: $425 \text{ kgm} = 1 \text{ Cal}$. In words: 425 kilogram-metres of mechanical work are worth one kilogram unit of heat. A kilogram-metre is the work of lifting one kilogram by one metre, and the kilogram unit of heat, the large calorie, is the heat that warms one kilogram of water by one degree. The intuition is that heat and work are two currencies of the same money, and 425 is the exchange rate. Now a calculation aloud. Warming one litre of water, which weighs one kilogram, from 20 to 30 degrees takes 10 large calories. In work that is $10 \times 425 = 4250$ kilogram-metres, enough to lift a 425-kilogram piano ten metres up. So a small amount of heat is a surprisingly large amount of work, which is why burning fuel can drive engines at all.

$$425 \text{ kgm} = 1 \text{ Cal}$$



$$1 \text{ kg} : 20^\circ \rightarrow 30^\circ \\ = 10 \text{ Cal}$$

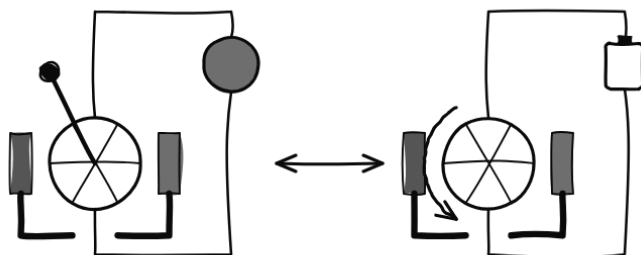


$$10 \times 425 = 4250 \text{ kgm}$$

Heat and Work Exchange

Electricity, too, trades with motion. Spin a Gramme dynamo, Mendeleev notes, and you get a current; pass a current through the same machine, and it spins. The conversion runs both ways, just as heat and work do. The electric motor in a kitchen blender and the generator in a power station are the same machine run in opposite directions. So chemical mechanics, he concludes, must take its main lines from the links between chemistry and physics. But the subject was still too complex and too new for a sound theory, or even a satisfying hypothesis, so he sets it aside as a branch of its own, physical chemistry.

CHEMISTRY FOLLOWS PHYSICS



TURN → CURRENT CURRENT → TURNS



**POWER-STATION
GENERATOR**



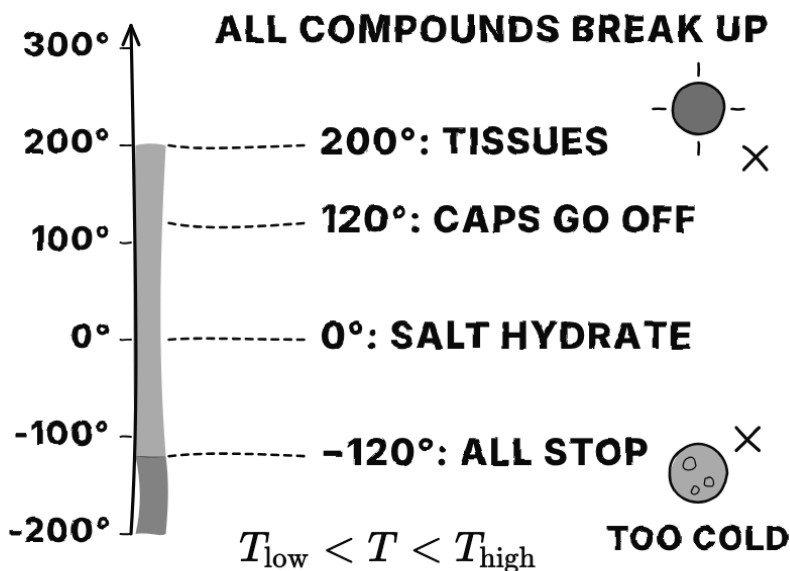
**CONDITIONS:
RED HEAT FIRST**



**BLENDER
MOTOR**

Motion and Current Both Ways

What he does lay out are the conditions. A reaction goes one way or another not only because of the masses, the composition and the affinities of the substances, but also because of the conditions they are in. Often a reaction needs conditions very different from those things meet in nature. That is the charcoal: it needs not only oxygen but also red heat. The glowing part combines with oxygen, the heat it gives off brings the next part to red heat, and only then does that part burn. Every reaction, Mendeleev says, goes only under certain physical and mechanical conditions, and the first of these is the degree of heat.



The Temperature Window

Combinations go only within definite limits of temperature. Burning is one example: it starts and continues only at red heat. A stranger one is that chlorine and common salt each form a compound with water only below 0°; above that the compound does not form, and if already made it falls wholly or partly apart.

Why should heat help a reaction along? Mendeleev gives two reasons. First, heat can melt or vaporise one of the substances, and a liquid or gas lets the particles come into fuller contact, which every reaction needs. Second, heat weakens cohesion, the bond between like particles, so the parts of the starting substances come apart more easily and are freer to form new compounds. And when a reaction

needs to absorb heat, as decompositions do, the need for heating is obvious.

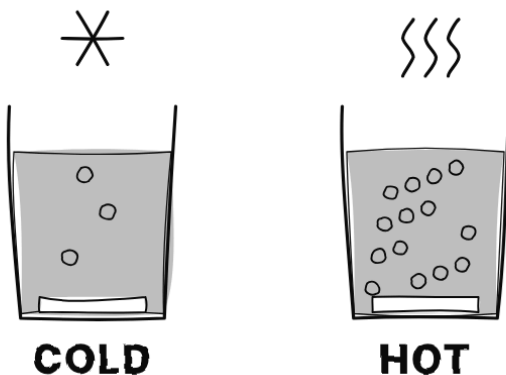
In fact, Mendeleev says, all compounds decompose if heated strongly enough. We have met examples: red mercury oxide falling into mercury and oxygen, and wood breaking apart in the heat. Some compounds need very little. The mercury fulminate in a gun's percussion cap decomposes at just over 120° . Many substances of animal and plant tissue decompose by 200° .

There is a lower edge to the window too. In great cold, reactions stop: plants halt their chemistry in winter. In 1892 Raoul Pictet used the boiling of liquefied gases to reach about -200° . Below -120° , he found, not even sulphuric acid and caustic soda react, nor sulphuric acid and sodium metal, though at room temperature these react violently. Even litmus, the dye that turns red in acid, changes colour only above -80° .

Let us put the window as a formula. For each reaction there is a lower limit T_{low} and an upper limit T_{high} , and the reaction goes only when $T_{\text{low}} < T < T_{\text{high}}$. In words: too cold and the particles are too sluggish to react; too hot and the compound falls apart as fast as it forms. For Pictet's acid and soda, the lower limit lies somewhere above -120° ; for the compound of salt and water, the upper limit is about 0° . And Mendeleev draws the striking conclusion: on the sun, where it is very hot, or on the moon, where it is very cold, many of the reactions we see every day on earth surely cannot happen at all.

Try it yourself

Put two teaspoons of baking soda into two glasses. Pour cold water from the fridge into one and a squeeze of lemon juice on top; do the same in the other glass with hot water from the kettle. Watch the fizzing: in the hot glass it is quick and lively, in the cold one slow and lazy. The reaction is the same, but its pace depends on the temperature, a small glimpse of the temperature window.



SAME REACTION, DIFFERENT PACE

Cold Glass, Hot Glass

Remember

Reactions produce motion, heat, light and electricity, and each of these can in turn change reactions, because all are forms of motion. Heat and work are exchanged at a fixed rate: 425 kilogram-metres of work equal one large calorie of heat. Every reaction needs its conditions, and the first is temperature, as charcoal burns only once it is red-hot. Heat helps reactions by melting or vaporising substances and by weakening cohesion, and strong enough heat decomposes every compound. Each reaction goes only inside a temperature window: Pictet found that below minus a hundred and twenty degrees even violent reactions stop.

Questions

1. Once one corner of a lump of charcoal is red-hot, why does the whole lump go on burning by itself?
 - a. Because the heat from the burning part brings the next part to red heat, and only red-hot charcoal burns
 - b. Because the flame spreads oxygen through the charcoal
 - c. Because charcoal burns at any temperature once lit
 - d. Because the air warms up and starts the reaction everywhere at once
2. Why can a reaction be changed by heat, light or electricity, as well as produce them?

- a. Because reactions are a kind of electricity
 - b. Because all phenomena of nature are different kinds of motion, visible and invisible
 - c. Because heat and light are substances that enter compounds
3. Which of these is a reason Mendeleev gives for why heating helps a reaction?
- a. Heat adds new simple bodies to the mixture
 - b. Heat makes the substances heavier
 - c. Heat weakens cohesion, so the parts of the starting substances separate more easily
 - d. Heat strengthens the bond between like particles
4. What did Pictet's experiments with liquefied gases show?
- a. That cold makes all reactions faster
 - b. That sulphuric acid and caustic soda react best when frozen
 - c. That litmus never changes colour in acid
 - d. That below about minus a hundred and twenty degrees even violent reactions do not happen

Answers

1. **a)** The glowing part combines with oxygen, and the heat it gives off brings the next part to red heat; only then does that part burn.
2. **b)** The influence runs both ways because all the phenomena of nature are different kinds of motion, the invisible ones being the motions of molecules.
3. **c)** Heat weakens cohesion, the bond between like particles, so the parts of the starting substances come apart more easily.

4. d) Below minus a hundred and twenty degrees not even sulphuric acid and caustic soda react, so every reaction has a lower temperature limit.

Worked examples

Heat as work Using the mechanical equivalent of heat, 425 kilogram-metres of work to one kilogram unit of heat, how much work corresponds to 6 units of heat?

The equivalent is an exchange rate: one unit of heat is worth 425 kilogram-metres of work.

So 6 units are worth 6 times as much.

$$6 \times 425 = 2550.$$

Answer: 2550 kilogram-metres

Practice

1. A machine does 3400 kilogram-metres of work, and all of it turns into heat. How many kilogram units of heat is that?

Hint: Divide the work by the rate, 425 kilogram-metres per unit of heat.

Answer: 8 units of heat, since $3400 / 425 = 8$.

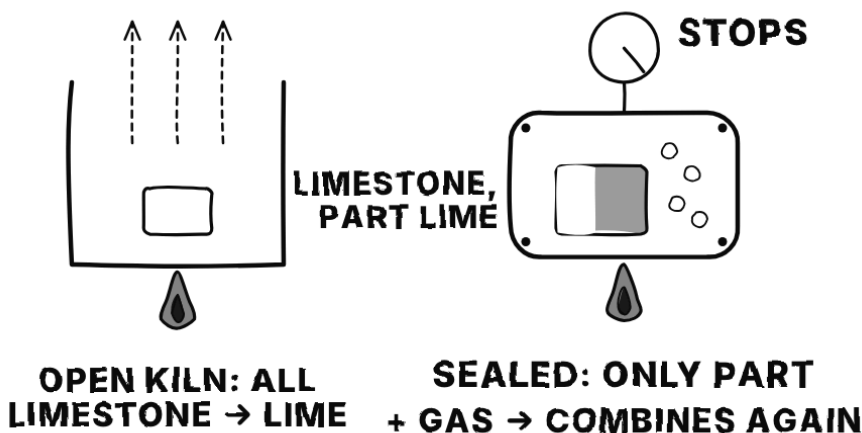
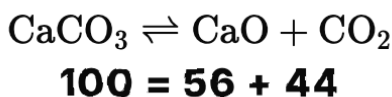
2. Mendeleev says many reactions seen on earth surely cannot happen on the sun or on the moon. Explain why, using what this part says about temperature.

Hint: Every reaction has a lower and an upper temperature limit.

Answer: Each reaction goes only within certain limits of temperature. On the sun it is so hot that compounds decompose, since all compounds decompose under strong enough heat; on the moon it is so cold that, as Pictet found, even violent reactions stop. So many earthly reactions fall outside their window there.

Half-Finished Decompositions and the Power of the Current

A lime kiln is a tall furnace filled with lumps of limestone, with a fire burning at its base. Heat it for a day, and every lump has turned into quicklime, while carbonic acid gas has gone up the chimney. Now imagine doing the same thing in a closed iron tube. Mendeleev describes exactly this: put limestone into a gun barrel, rivet the end shut, and heat it red. This time only part of the stone decomposes, and the rest stays limestone, however long you wait. What is different?



Open Kiln, Sealed Barrel

The answer is a phenomenon Mendeleev calls dissociation. Take a compound that can be formed back from its own products, a reversible one, and heat it. At a certain temperature it begins to decompose, but in a closed space it does not go all the way. Only a share breaks up; the rest stays untouched. Raise the temperature, and the share grows; at each temperature, for a given volume, there is a fixed ratio of decomposed to untouched substance, until at last a temperature is reached where the compound falls apart completely. This incomplete, temperature-dependent decomposition is dissociation, and it has a starting temperature and an ending temperature.

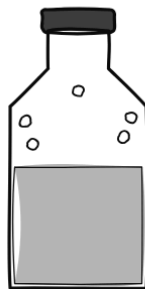
For limestone the reaction, in today's notation, is $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. In words: limestone breaks into lime and carbonic acid gas, and lime and the gas can join again into limestone. By weight, 100 grams of limestone give 56 grams of lime and 44 grams of gas, since $56 + 44 = 100$. In the open kiln the gas escapes as fast as it forms, so the reverse road is never taken and all 100 grams go to lime. In the sealed barrel the gas cannot leave. Its pressure builds until it reaches the greatest pressure that belongs to that temperature, called the dissociation pressure, and then decomposition stops. Pump in more gas, and lime and gas start combining again; let some out, and decomposition starts again.

Mendeleev's comparison makes this easy to picture: dissociation is just like evaporation. Leave water in a sealed jar, and it evaporates until the vapour above it reaches the greatest pressure for that temperature; then evaporation stops. Push in more vapour, and some condenses back to liquid; take some out, and more water evaporates. A closed bottle of water on a warm windowsill fogs on the inside but never dries out, for exactly this reason, while an open glass beside it

slowly empties. The kiln is the open glass, and the gun barrel is the closed bottle. These ideas, Mendeleev says, were brought into science by Henri Sainte-Claire Deville, and he will return to them often.



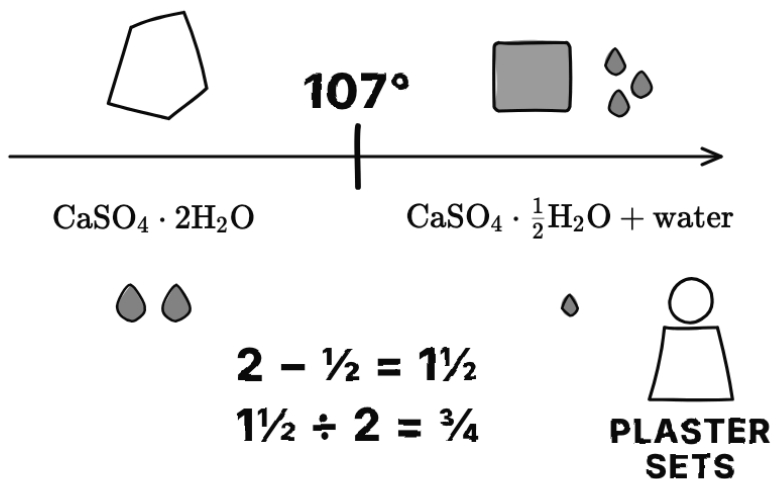
**OPEN: EMPTIES
LIKE THE KILN
SAINTE-CLAIRE DEVILLE**



**CLOSED: STOPS
LIKE THE BARREL
SAINTE-CLAIRE DEVILLE**

Like Water in a Closed Bottle

Two more points follow. First, the separated parts combine most easily near the temperature at which dissociation begins; so the temperature where a compound starts to fall apart is close to the temperature where its parts start to react. Second, some changes happen at one sharp temperature, like melting or boiling. Above it the compound breaks up; below it, it forms again; and the switch can be seen on a thermometer or by a sudden change of volume measured with a dilatometer.

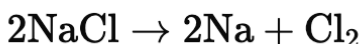
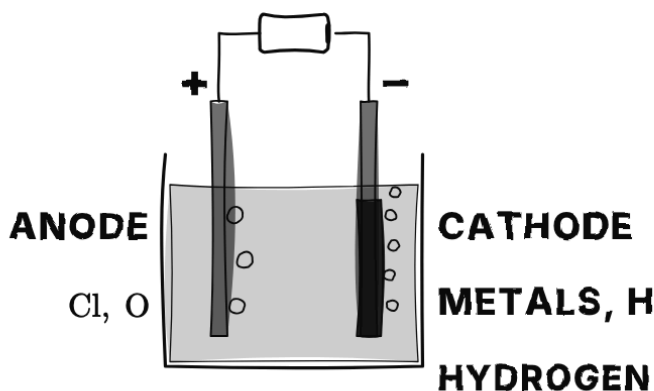


Gypsum at 107 Degrees

His example is gypsum, the mineral with two waters, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In a closed space, at 107° , it breaks up completely into a wet paste: a salt with only half a water, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and liquid water. Let us count the water. Before, there were 2 waters for each unit; after, the salt keeps $\frac{1}{2}$. So the water set free is $2 - \frac{1}{2} = 1\frac{1}{2}$, and as a share of the original, $1\frac{1}{2} / 2 = \frac{3}{4}$, exactly the three quarters Mendeleev reports. Cool it below 107° , and the two-water salt forms again. Plaster of Paris is this half-water salt; mix it with water, and it sets hard as it takes the water back, which is why plaster casts can be poured at room temperature.

Now the second agent of this part: electricity. Its effect, Mendeleev says, is very like that of heat. Most compounds that carry a galvanic

current are decomposed by it, and near the conditions of decomposition, combination also happens, just as with heating. Electricity, like heat, is a kind of molecular motion. But it has one great advantage: it can take compounds apart at ordinary temperature, and it can split even the most stable ones.



The Current Splits Salt

And it shows something heat never could: the parts appear at different poles. The current enters and leaves the substance through two electrodes. At the positive pole, the anode, appear the substances called electronegative: mostly non-metals, such as chlorine and oxygen, and acids and things like them. At the negative pole, the cathode, appear the electropositive ones: metals, hydrogen and products like them, which are called ions. So for common salt, broken

by a current, in today's notation, $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$: sodium goes to the cathode, chlorine to the anode.

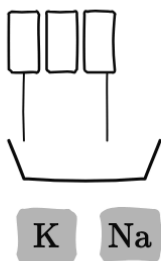
Try it yourself

Fill a glass with warm water and stir in a teaspoon of salt.

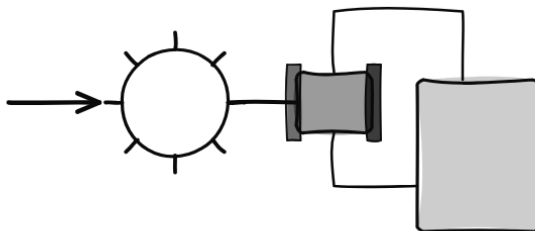
Connect two pencil leads, or two bare wires, to the terminals of a 9-volt battery and dip their free ends in the water, a little apart.

Watch the wire joined to the minus terminal: a stream of fine bubbles rises from it, hydrogen, as Mendeleev says, appearing at the negative pole. Do this only for a minute, in a ventilated room, and do not smell the water near the other wire: it can give off a little chlorine.

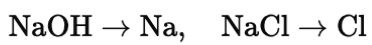
This method made history. Many simple bodies were first obtained with the current. Most famous are potassium and sodium: Lavoisier and his contemporaries could not break down their compounds with oxygen, but the Englishman Davy passed a current through them and found the metals appearing at the negative pole. For a long time this stayed a laboratory feat. Then dynamos made current cheap, driven by burning fuel or by water and other engines, and Davy's method became a factory method. Sodium was made from molten caustic soda, NaOH , written NaHO in Mendeleev's day, and chlorine from solutions of common salt.



DAVY



FACTORY



From Davy's Bench to the Factory

Remember

Dissociation is the incomplete decomposition of a reversible compound, with a fixed share broken up at each temperature in a closed space. If the products escape, as from an open lime kiln, decomposition goes to the end; if they are held in, as in a sealed barrel, it stops at the dissociation pressure, just as evaporation stops in a closed jar. Some changes happen at one sharp temperature, like gypsum at a hundred and seven degrees, which loses three quarters of its water and takes it back on cooling. An electric current decomposes compounds even at room temperature, with non-metals at the positive pole and metals and hydrogen at the negative one. Davy obtained potassium and sodium this way, and cheap current from dynamos made it a factory method for metals and chlorine.

Questions

1. Why does limestone decompose completely in an open kiln but only partly in a sealed gun barrel?
 - a. In the kiln the gas escapes; in the barrel it stays, and decomposition stops when its pressure reaches the dissociation pressure
 - b. The barrel cannot be heated as strongly as the kiln
 - c. Iron reacts with the limestone and protects it
 - d. The kiln adds oxygen, which the barrel lacks

2. In the sealed barrel, more carbonic acid gas is pumped in at the same temperature. What happens?
 - a. More limestone decomposes
 - b. Lime and gas start combining back into limestone
 - c. Nothing changes
 - d. The lime melts
3. What advantage does an electric current have over heat for decomposing compounds?
 - a. It adds new elements to the compound
 - b. It only works on weak compounds
 - c. It works at ordinary temperature and can split even the most stable compounds
4. When common salt is decomposed by a current, where does the sodium appear, and why does that fit the pattern?
 - a. At the anode, because metals are electronegative
 - b. At both poles, because salt holds two elements
 - c. Nowhere, because sodium stays dissolved
 - d. At the cathode, because metals are electropositive

Answers

1. **a)** In the sealed barrel the gas cannot leave; its pressure builds to the greatest pressure for that temperature, and then decomposition stops.
2. **b)** Pump in more gas, and lime and gas start combining again; let some out, and decomposition starts again.
3. **c)** Electricity can take compounds apart at ordinary temperature, and it can split even the most stable ones.

4. d) Metals and hydrogen appear at the negative pole, the cathode; chlorine goes to the anode.

Worked examples

Water lost by gypsum Gypsum, the calcium sulphate salt with two waters, breaks up at 107° in a closed space into the salt with half a water and liquid water. What share of its water is set free?

Before the change each unit holds 2 waters.

After it, the new salt keeps $\frac{1}{2}$ water.

So the water set free is $2 - \frac{1}{2} = 1\frac{1}{2}$ waters.

As a share of the original water, $1\frac{1}{2} / 2 = \frac{3}{4}$.

Answer: Three quarters of the water

Practice

1. Explain in your own words why dissociation is compared with evaporation, using the open kiln and the sealed barrel.

Hint: What happens when the vapour, or the gas, can escape, and when it cannot?

Answer: In both, if the vapour or gas is not removed, its pressure rises to the greatest value fixed by the temperature and the process stops; adding more makes it go back, removing some lets it continue. The open kiln is like an open glass of water, where everything goes; the sealed barrel is like a closed jar, where the change stops part way.

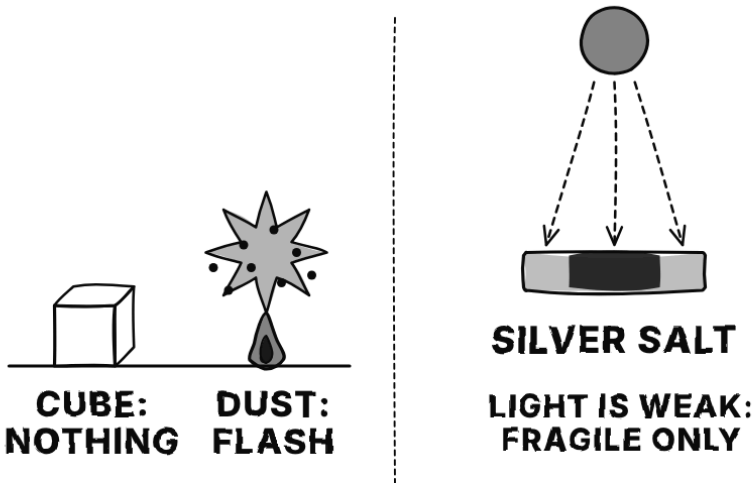
2. Lavoisier could not break down the compounds of potassium and sodium with oxygen. Explain how Davy did, and why the method later moved into factories.

Hint: Think of which pole metals go to, and what made current cheap.

Answer: Davy passed a galvanic current through these compounds, and the metals appeared at the negative pole. Later, dynamo machines driven by fuel or water power made current cheap, so his method became a profitable way to make sodium from molten caustic soda and chlorine from salt solutions.

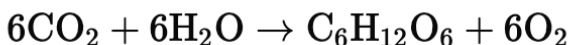
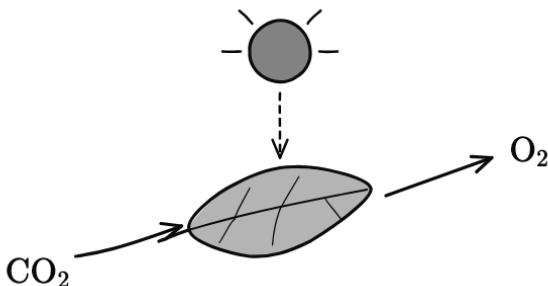
Light, Blows, Time and Touch

Leave a sugar cube on the table, and nothing happens to it for years. Grind the same sugar to a fine dust and blow it in a cloud through a flame, and it flashes. Flour mills and sugar factories take great care with dust for exactly this reason: a cloud of fine powder can burn in an instant. Same substance, same air, same flame; the only difference is how much of the sugar touches the air. This last part is about such conditions, the ones besides heat and electricity that steer a reaction: light, blows and pressure, time, and contact.



Cube and Dust; Light on Silver

Light comes first. Some unstable compounds fall apart when light falls on them, and photography rests on this, with salts of silver darkening where light strikes. But light is a weak agent, Mendeleev says, because the mechanical work of its vibrations is very small, so under ordinary conditions it can only break fragile compounds. And yet in plants light does something that was, in his day, an unsolved riddle. Carbonic acid gas is so stable that heat and current hardly touch it, yet in green leaves, in light, it is broken down and oxygen is given off. In today's notation the overall change is $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$. In words: carbon dioxide and water, driven by light, become sugar and oxygen. Count the oxygens to see that the books balance: on the left $6 \times 2 + 6 \times 1 = 18$; on the right $6 + 6 \times 2 = 18$. Light can also start combinations: chlorine and hydrogen combine not only when heated but when light shines on them.

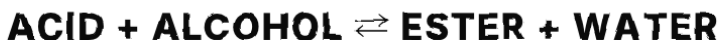
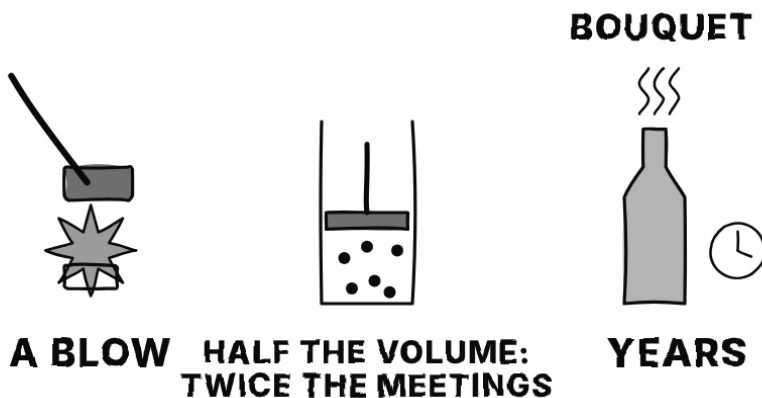


$$\text{O} : 6 \times 2 + 6 = 18 = 6 + 6 \times 2$$



Light in a Green Leaf

Next, mechanical influences, which can also drive both combination and decomposition. Some substances decompose from a mere rub or a blow. Nitrogen iodide, a compound of nitrogen, iodine and hydrogen, is one; the mercury fulminate in a gun's percussion cap, which goes off when the hammer strikes it, is another. Rubbing can make sulphur burn using the oxygen held in Berthollet's salt. The head of a safety match works on the same idea: friction against the box starts a reaction between a sulphur-type fuel and an oxygen-rich salt.



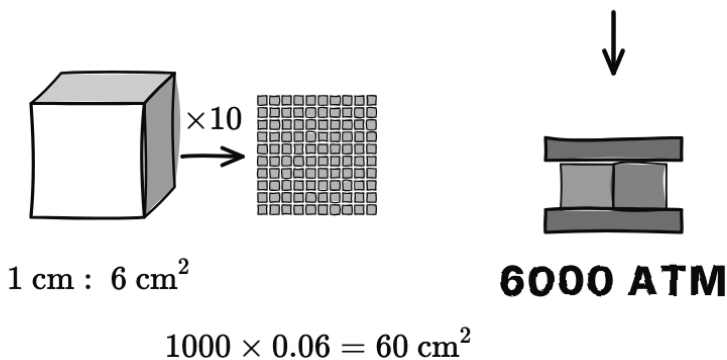
Blows, Pressure and Time

Pressure matters too, together with temperature, and most of all for gases, whose volume changes greatly with pressure. Squeeze a gas into half its volume, and its particles meet the particles of another substance about twice as often. So compressed hydrogen acts more energetically on iodine and on solutions of many salts, given a suitable temperature.

Then time. Every reaction needs time in two ways. First, the substances must be brought together, and that movement has a limited speed: a lump of coal burns at its surface, and only as fast as fresh surface is exposed and fresh air flows in. Second, even after full contact, the inner rearrangement that is the reaction itself runs at its own definite speed. Mendeleev's familiar example is the ageing of

wine. Young wine contains acids and alcohol separately; as the wine is kept, they slowly react by double decomposition to give water and fragrant compound ethers, which we now call esters, and these make the "bouquet". The reaction is reversible, acid + alcohol $\rightleftharpoons$ ester + water, and at cellar temperature its speed is plainly limited, depending on the warmth and other conditions. Most of the vivid reactions a beginner meets run so fast that time can be ignored, but slow ones like this are many.

Last, and perhaps most surprising, is the state of contact. To increase the number of points of contact is, other things being equal, to make a reaction go harder. Sulphuric acid sitting quietly under olefiant gas, which we call ethylene, does not absorb it, but shake the two together for a long time and it does, because the points of contact are multiplied enormously. Solids must be ground as finely as possible and mixed well to react fully and quickly.



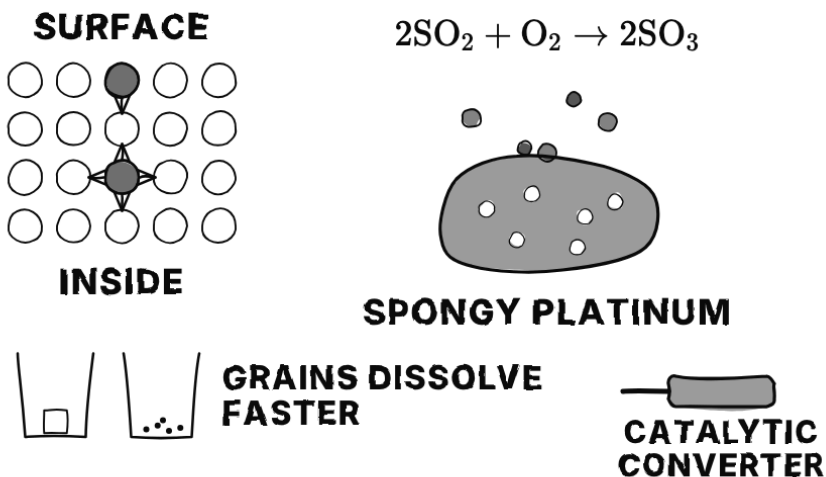
Ten Times the Surface

Let us put a number on what grinding does. A cube of sugar one centimetre on each side has a surface of $6 \times 1 \times 1 = 6$ square centimetres. Cut it into little cubes one millimetre on a side: there are $10 \times 10 \times 10 = 1000$ of them, each with a surface of $6 \times 0.1 \times 0.1 = 0.06$ square centimetres. Together that is $1000 \times 0.06 = 60$ square centimetres, ten times the surface of the whole cube. In words: each time you cut the pieces ten times smaller, the surface that can touch the air or another substance grows tenfold, and that is why the cloud of sugar dust can flash.

The Belgian chemist Spring pushed contact to an extreme. Powders of solids that do not react at room temperature, he showed, will react under great pressure: at 6000 atmospheres sulphur combines with

many metals, and powders of many metals form alloys, all at ordinary temperature. Mendeleev's explanation is the increase in the points and planes of contact, and it shows that solids, like liquids and gases, have inner motion and mobile particles.

Then he adds a deep idea. A particle deep inside a substance is pulled on from all sides by its neighbours; a particle at the surface is pulled from one side only. So matter at a surface is in a different state, and where it touches another body that state can be changed as if the temperature had been raised. This explains a whole class of reactions that happen only in the presence of certain bodies, which Mendeleev calls contact reactions, or catalysis. Porous and powdery bodies do this best, above all spongy platinum and charcoal. Sulphurous gas does not combine directly with oxygen, but over spongy platinum it does, giving off heat: in today's notation, $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$, with the platinum unchanged at the end. The catalytic converter under a modern car uses the same trick, with a thin film of platinum-group metals helping exhaust gases react as they pass.



Surfaces and Catalysis

Try it yourself

Drop a whole sugar cube into a glass of cold water and a teaspoon of granulated sugar into another, and do not stir. Note how long each takes to disappear. The granulated sugar dissolves far faster, though it is the same substance in the same water. Its many small grains offer much more surface, the points of contact that Mendeleev says speed every reaction.

Mendeleev ends his introduction with a short reflection. All these general ideas only take on their real meaning once you meet the particular substances and reactions, which is where the book now

goes. Even so, it was necessary to begin with the broadest principles, the conservation of matter and of energy, because only with them can the study of particulars be manageable and fruitful. So this course ends where his chemistry begins: with the balance in one hand and the law of conservation in the other.

Remember

Light breaks fragile compounds, as in photography, and in plants it splits even stable carbonic acid gas, giving off oxygen; it can also start combinations, like chlorine with hydrogen. Blows, rubbing and pressure can start reactions, from percussion caps to compressed hydrogen acting on iodine. Reactions take time, both for the substances to meet and for the rearrangement itself, as in the slow ageing of wine. More contact means a faster reaction: grinding a cube into thousandth parts gives ten times the surface, and Spring made powders react under great pressure. Surfaces such as spongy platinum can make substances react that otherwise would not, and all of this rests on the conservation of matter and energy.

Questions

1. Why can light, under ordinary conditions, decompose only fragile compounds?
 - a. Because the mechanical work of the vibrations of light is very small

- b. Because light only reaches the surface of a body
 - c. Because light acts only on silver
 - d. Because light causes combinations, never decompositions
2. Why does compressing a gas make it react more energetically with another substance?
- a. Because pressure turns the gas into a liquid
 - b. Because its particles meet the particles of the other substance more often
 - c. Because pressure adds heat to the gas
3. Sulphuric acid absorbs olefiant gas only after long shaking. What is the reason?
- a. Shaking warms the acid
 - b. Shaking makes the gas heavier
 - c. Shaking multiplies the points of contact enormously
 - d. Shaking removes air from the vessel
4. How does Mendeleev explain why spongy platinum makes sulphurous gas combine with oxygen?
- a. The platinum combines with the oxygen and is used up
 - b. The platinum gives off its own heat
 - c. The platinum supplies extra sulphur
 - d. At a surface particles are pulled from one side only, so matter touching it is changed as if heated

Answers

1. a) Light is a weak agent because the mechanical work of its vibrations is very small, so it can only break fragile compounds.

2. **b)** A gas's volume changes greatly with pressure, so squeezed into a smaller volume its particles meet those of another substance more often.
3. **c)** Shaking the two together multiplies the points of contact enormously, and more contact makes a reaction go harder.
4. **d)** Matter at a surface is in a different state, and where it touches another body that state can be changed as if the temperature had been raised; this is catalysis.

Practice

1. Explain in your own words the two ways in which a reaction needs time, using the burning of a solid and the ageing of wine.

Hint: One is about bringing the substances together; the other is about what happens once they touch.

Answer: First, the substances must be brought together, which has a limited speed: a solid burns at its surface, only as fast as fresh surface and fresh air arrive. Second, even after full contact the reaction itself runs at its own definite speed: in wine, the acids and alcohol slowly react to give water and fragrant compound ethers, a reversible reaction that takes a long time at ordinary temperature.

2. Spring made sulphur combine with metals at ordinary temperature. How did he do it, and what does it show about solids?

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

Answer: He pressed the powders at about 6000 atmospheres, which increased the points and planes of contact between them. It shows that solids, like liquids and gases, have inner motion and mobile particles, so they can react once contact is close enough.

3. Why does Mendeleev begin his book with general principles, the conservation of matter and of energy, before the particular

substances?

Hint: What would the study of particulars be like without them?

Answer: The general ideas take on their full meaning only with the particular substances, but the broadest principles had to come first, because only by recognising the conservation of matter and of energy can the study of particulars be manageable and fruitful.