S. Venetsky

ON RARE AND SCATTERED METALS

Tales about Metals

MIR Publishers
Moscow

С. И. Венецкий

О РЕДКИХ И РАССЕЯНИЫХ

Рассказы о металлах

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S. I. Venetsky

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N. G. Kittell

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The Russian Alphabet and Transliteration

Аа	a	Кк	k	Хх	kh
Бб	b	Лл	l	Цц	ts
Вв	v	Мм	m	Чч	ch
Гг	g	Нн	n	Шш	sh
Дд	d	Оо	o	Щщ	shch
Ее	e	Пп	p	Ъъ	”
Ёе	e	Рр	r	Ыы	y
Жж	zh	СС	s	Ьь	’
Зз	z	Тт	t	Ээ	e
Ии	i	Уу	u	Юю	yu
Йи	y	Фф	f	Яя	ya

TO THE READER

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На английском языке

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Ours is an age of incredible breakthroughs in science and technology: man has blazed a trail into outer space, harnessed the energy of the atomic nucleus, built "thinking" machines and unravelled the mystery of the living cell.

Humanity is moving into ever new and fascinating fields, but there is one field of activity which, while being old as the hills, is no less fascinating. This field is metallurgy, the production and working of metals and alloys.

At the dawn of civilization people were familiar with only a few metals. But as ages passed and ever more new elements were discovered, the range of useful metals extended as well. In the case of some metals scientists and engineers did not take long to acknowledge and appreciate them, with others, it took years before they began to be applied. There were valid reasons for their "idleness". First, the content of many of them in the earth's crust is minute and therefore, it is extremely difficult to extract them; some have no minerals of their own and occur only as impurities in other metals (such "scattered" elements belong to the group of trace elements). Second, up to a certain period science lacked information on most metals and since those we are going to discuss were used very rarely in industry, they were called rare metals.

The explosive development of technology is the hallmark of the 20th century, a time when instrument-making, chemistry, aviation, rocketry, electronics and nuclear power — all started to place orders for new materials with unique properties. This is what prompted scientists to delve deeper into the world of rare metals. A careful study of those "recluses" revealed that many of them were quite "gifted". Thus began the advent of rare metals in industry.

It would probably be correct to say that today not a single new area of technology can do without rare metals, their alloys or compounds. For example, fine-filament suspensions for navigation instruments of high precision are made from rhenium alloys; gallium goes into the manufacture of so-called liquid seals in vacuum equipment and high-temperature thermometers and pressure gauges; cesium is the most important component of photocells used in flaw detectors and some other instruments; hafnium is the material from which control rods of nuclear reactors are made and is also promising as a component of superalloys being developed for aviation and rocketry; a thin layer of indium deposited on ball-bearings protects them from erosion and increases their service life. Such examples could be listed indefinitely.

This book tells about some rare metals (including those called trace elements) and can be regarded as a second part of S. I. Venetsky's *Tales About Metals* (It was published in English by Mir Publishers, Moscow, in 1981).

The author follows the same principle as in his previous work: rather than giving the reader any exhaustive information about every chemical element he describes, to tell him some interesting facts, curious incidents and tales associated with rare metals, to tell about the thorny path of any major scientific discovery and about some paths yet to be trodden in the amazing world of metals.

The book is "peopled" by real and fictitious characters. Along with many outstanding scientists, it alludes to Napoleon, Agatha Christie, Karel Capek and Sherlock Holmes. The stories associated with them are a background against which the author introduces his reader to achievements in metallurgy, physics and chemistry, to advances in the development of new processes of making metals and materials and to new instruments. It was only recently that experiments in space materials science were carried out on board the *Salyut-6* space station, but they too are mentioned in the book.

Many scientists and engineers make their first steps to the summits of science and engineering under the influence of popular science literature. It is my firm belief that this book will also help many young people with the crucial choice — their future occupation.

Academician A. F. Belov

Ga

THE TRIUMPH OF A GREAT LAW (GALLIUM)

Do not hasten to draw conclusions!— The first piece of evidence.— Irony of fate.— A violet stranger.— Was it a cock?— A scientific argument.— Different fates.— Shameful "discrimination".— A poor relative.— The wealth is hidden in the waste.— Gallium on the palm of a hand.— There will be no fire.— Lamps become better.— A great eccentric.— Beyond compare.— Not a good comrade.— Exceptional gifts.— No fool.— Experiments in space.— Why is the Sun shining?

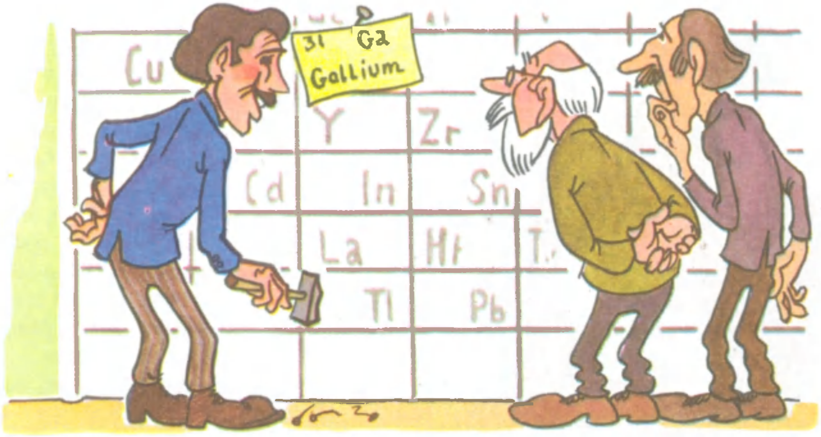
Dmitri Mendeleyev's discovery, in March 1869, of a periodic law which governs the behaviour of absolutely all chemical elements was given a hostile reception by some scientists. Even a chemist of such eminence as Robert Bunsen, one of the creators of spectral analysis, made this caustic remark: "One can draw any number of such generalizations on the basis of figures printed in stock-exchange bulletins."

Later Bunsen must have regretted his ill-considered remark on more than one occasion, but back in 1869 Mendeleyev was yet to prove his law. And he did prove it brilliantly. The greatness of the periodic law consisted in that it not only generalized and put in strict order whatever information about chemical elements scientists had at their disposal, but became something of a compass to the multi-thousand-strong army of experimenters seeking new islands in the boundless sea of chemistry: new elements, new bricks of the universe. On the basis of the periodic law Mendeleyev was able to predict the discovery of more than a dozen elements.

The first to prove Mendeleyev's correctness was gallium.

At the end of 1870, addressing a sitting of the Russian Physical and Chemical Society, Mendeleyev said that in the fifth row of the third group of elements there was a place for an element which was yet undiscovered but which definitely existed somewhere in nature. He described the properties of the new element in much detail and gave it the arbitrary name eka-aluminium (its place in the table of elements being beneath aluminium). He even expressed confidence that it would be discovered by spectral analysis. (There is irony of fate for you: could Bunsen ever expect the spectral method he worked out to play such a mean trick on him and furnish irrefutable proof of the fallacy of his premature denial of the periodic law?)

The news of discovery of the predicted element was not long in coming. In 1875 the French chemist Lecoq de Boisbaudran made a spectral study of a specimen of zinc blende, a well-known mineral



from Pieerefitte in the Pyrenees, discovering a stranger — a violet line which was an indicator that the mineral contained an unknown chemical element.

But it was one thing to discover the line and quite another, to isolate the element responsible for it. Not an easy task at all, considering that the content of the unknown element in zinc blende was minute. But the chemist was successful: his numerous experiments yielded a grain of the new metal weighing 0.1 gram.

The most difficult part over, Lecoq de Boisbaudran now had to give his metal a name. He called it gallium in honour of his country (Gallia is the Latin for France). True, some wicked tongues soon began to assert that gallium was the chemist's cleverly concealed hint at his own name: *gallus* in Latin means a cock and the French for cock is *le coq*, which makes the connection with Lecoq de Boisbaudran only too obvious, they said.

Soon the news of the discovery of gallium was published in a paper of the French Academy of Sciences. When it reached Mendeleyev he immediately realized that this was the eka-aluminium to which he had already assigned a place in the table of elements. In his letter to the French Academy Mendeleyev wrote: "... the method by which it was discovered and isolated and also the few properties described allow me to suggest that the metal is nothing else but eka-aluminium".

Indeed, the properties of the theoretical eka-aluminium and the really existing gallium were amazingly identical. The only difference was in their density: according to Mendeleyev, it had to be around 6 g/cm^3 and the French chemist estimated it to be 4.7 grams. Who was correct? The one who had never even seen the new metal or the other who not only held it on his palm but carried out various experiments with it? It was not the first time in the history of science that theory clashed with practice, the mind questioned the experiment.

To prove he was right Boisbaudran once more isolated a few grains of gallium, carefully cleaned them and made a new study. This time he found that the density of gallium was really close to 6 and publicly acknowledged the correctness of his Russian colleague. He wrote: "It seems there is no need to point out the exceptional importance the establishment of density of the new element has to confirming Mendeleyev's theoretical conclusions."

There is much similarity in the history of many metals. But just as among hundreds of people you know you will not find two whose biographies are identical, you will not find two metals with identical histories. Even twins like zirconium and hafnium or tantalum and niobium have different stories to tell. But the early stages in the life of most metals were equally uneventful: they patiently waited for some work to be found for them. Some were lucky and only a few years after discovery were leading active lives. For others the period of waiting lasted a long time. Gallium was among the unfortunate ones.

More than half a century had passed since Lecoq de Boisbaudran had announced to the world the discovery of gallium but the industrial world was still ignoring it. The 14th volume of the Great Soviet Encyclopaedia (1st Ed.) published in 1929 had exactly four words on the application of gallium: "Not used in technology". And that was that.

But what can explain such discrimination? Could it be that the metal which had played such an outstanding role in confirming the periodic law would find no other use but taking up residence in the 31st square of the table of elements? Could it be that it did not possess a single property capable of arousing the interest of designers, inventors and scientists?

The properties of gallium, as you will soon see for yourself, had nothing to do with it. But perhaps nature's stock of this element was too small and that explained all its misfortunes? Alas, that was not so either. The earth's crust contains tens of times more gallium than say, tantalum or tungsten, and hundreds of times more than mercury or silver.

The point is that, like some scattered elements, gallium did not "bother" to create its own deposits. Furthermore, it has practically no minerals of its own. It was fairly recently that the first gallium mineral was discovered in South-East Africa. Hallite, as the mineral is called, contains up to 37 per cent of gallium. But as a rule, hardly appreciable quantities of this element (a few hundredths of one per cent) are found "living" like "poor relatives" with aluminium and more seldom, with iron, zinc, copper and some other metals. It has been found that coal ash is comparatively rich in gallium. According to British scientists, one ton of coal mined in the British Isles contains an average of five grams of gallium. Is that all? It seems even this minute concentration is believed sufficient for its industrial recovery. (Everything is relative: iron ore, one ton of which contains some 300 to 400 kilograms of iron, is generally considered poor.)

The production of gallium has been expanding at a slow rate. The first 50 kilograms of this metal were produced in Germany in 1932. Some twenty-five years later gallium production had reached only 350 kilograms. Though modern output is measured in tons, even such a scarce metal as rhenium, the content of which in the earth's crust is tens of thousands of times less than that of gallium, has left it far behind in quantities produced.

The main source of gallium are... the waste products of the aluminium industry. But do not hurry to conclude that gallium is a cheap metal. Though the raw material costs nothing, the process of recovery of the metal is so complex (even the extraction from aluminium) that it turns out to be one of the most expensive metals on the world market. In the middle of the 1950s one kilogram of gallium cost 3 000 dollars — almost three times the price of gold. Just think, an ingot easily held on the palm of a hand at such a price!

As a matter of fact, holding gallium on one's palm is exactly what we shouldn't advise one to do, and not only because it is not a very reliable container for a very precious metal, but because the warmth of the human body is enough to transform it into a liquid state: the melting point of this silvery, soft metal (you can cut it with a knife) is extraordinarily low, 29.8°C. In this respect it is inferior only to the restless mercury which becomes immobile only at minus 40°C, and to some extent, to cesium melting at 28.5°C. Another reason why gallium

should not be held in a hand is that it is rather toxic (more so than mercury) and holding it may cause unpleasant consequences.

Its low melting point makes gallium the base of many fusible alloys. For example, an alloy of gallium (67 per cent) with indium (20.5 per cent) and tin (12.5 per cent) cannot remain solid even at room temperature: its melting point is 10.6° C. Such alloys have an extensive use in engineering, in particular, in fire-alarm systems. Once the air in the building warms up to a certain point, the gallium-alloy column fixed in a relay begins to melt, closing the electrical contacts and giving a sound or a light alarm signal. This device is much more reliable than any human guard.

Low-melting gallium alloys (and gallium itself) are also characterized by good wetting properties, which is why they are widely applied instead of mercury in vacuum seals. Gallium seals maintain a vacuum more effectively than mercury ones.

Alloys of gallium with indium and tin are used as lubricants, interlayers in joining parts made of quartz, glass and ceramics and also for pressure bonding. A gallium-indium coating of ball bearings considerably prolongs their service life. As mentioned earlier, gallium is very toxic, but in company with nickel and cobalt it fails to demonstrate its poisonous nature and is even used for dental fillings of high quality.

The cathodes in the ultra-violet lamps applied in medicine, which were formerly made from mercury, are now made from an alloy of aluminium with gallium. It has been found that this alloy is much better suited for the job as its flux contains more ultra-violet rays.

Most metals melt and solidify at the same temperature. The unique property of gallium is that it can remain liquid for months in a supercooled state. If a drop of gallium is left on ice it will not solidify for a long time. But when it finally does its volume will have expanded considerably. Therefore, metal or ceramic containers must not be filled with liquid gallium — they will burst as the metal becomes solid. It is usually stored in small gelatin or rubber cylinders. It has been suggested that the ability of gallium to grow in volume on solidification (all the other metals except antimony and bismuth "lose weight" as they transform from the liquid to solid state) should be used in ultrahigh pressure equipment.

But the main advantage of gallium is that it remains liquid over a vast temperature range, and here no other low melting metal can compare with it. Molten gallium begins to boil only heated to a temperature of 2 230°C. It is this amazing property that determines its main role in technology — high-temperature thermometers and pressure gauges. Gallium thermometers can be used for temperatures of 1 000°C and over, a level mercury thermometers cannot even approach: mercury boils already at 357°C.

The low melting point combined with the wide temperature range of its melt makes gallium a potential heat-transfer agent for nuclear reactors. But liquid gallium is not a good comrade to structural materials with which it might come into contact in the reactor: at high temperatures it dissolves and destroys most metals and alloys. This is why at present the important role of heat-transfer agent is usually played by sodium and potassium. But it is possible that scientists will find a way of coping with this problem: it has been found, for instance, that tantalum and tungsten easily survive the contact with gallium even at 1 000°C. It is an interesting fact that small additions of "aggressive" gallium (up to 5 per cent) to magnesium enhance the latter's corrosion resistance and strength.

Another interesting fact is that electric resistance of gallium crystals depends to a considerable degree on whether the current is passed through their horizontal or vertical axes. The maximum-minimum resistance ratio is 7, which is far greater than that of any other metal. The same is true of its heat expansion coefficient which changes by a factor of three depending on the current direction.

Gallium's outstanding ability to reflect light explains its successful application in the manufacture of mirrors, and it must be stressed, that gallium mirrors do not dim even at high temperatures. The oxide of the metal is essential for production of special glasses characterized by a high refractive index, allowing for a free transmission of infrared rays.

Super-pure gallium (no less than 99.999 per cent) serves as an alloy addition to germanium and silicon, increasing their semiconducting properties. Not long ago gallium itself was shown to be "no fool" in this respect. Some of its compounds — with antimony, phosphorus, and especially, arsenic — reveal semiconducting qualities.

These properties are strikingly demonstrated in heterojunctions ensuring high efficiency of semiconductor instruments. A heterojunction is a junction between two semiconductors with different chemical characteristics formed in a single crystal. Scientists have long since theoretically proved that this kind of "life under the same roof" holds interesting prospects for semiconductor engineering. The main difficulty lay in selecting a pair of materials for such "coexistence". Experimenters tried dozens of various combinations but all of them were far from ideal and only too often demonstrated open incompatibility. It was then suggested that the arsenides of gallium and aluminium could be a likely combination. Their crystalline lattices were similar like two drops of water and that was encouraging. But a new obstacle arose: in a humid atmosphere aluminium arsenide was so unstable that it became decomposed before one's very eyes.

Was it final defeat? Gallium saved the situation: atoms of gallium introduced in aluminium arsenide gave it adequate stability. The problem of heterojunctions was solved and numerous sophisticated instruments were designed on their basis.

The field of application of gallium compounds is constantly extending. Today one comes across them in computers, radars, thermocouples in solar batteries and in semiconductor devices for rocket-borne equipment. They are used in lasers and luminescent substances, and also as a strong catalyst involved in many important processes in organic chemistry.

Only recently the fictitious "engineer Garin's hyperbolloid" (a controlled concentrated ray of light invented by the main character of Alexey Tolstoy's well-known novel) seemed pure fantasy and the "hyperbolloids" of today, the lasers, are now becoming quite common. Gallium arsenide was one of the first laser materials. According to Western specialists, the simple, compact and effective lasers based on gallium arsenide were proposed for space apparatus, particularly for communications between the ship and the astronauts during their extravehicular activity, or between two space stations travelling in near space. There were also plans to use such a laser for the ship attitude control during the "landing" on the Moon.

Owing to weightlessness outer space is a unique setting for extensive technological experimentation. Interesting results were reported from the American *Skylab* whose crew succeeded in growing a gallium arsenide crystal 25-mm long. Here on earth it has yet been impossible to grow a crystal longer than two or three millimetres. Successful experiments along the same lines were also carried out on board the Soviet *Salyut-6*. Apart from that, the Soviet spacemen experimented with alloying gallium and molybdenum (by means of an installation called *Splav*). The point is that molybdenum is almost twice as heavy as gallium and under ordinary conditions the two cannot mix evenly: when the melt solidifies its upper layers appear to be rich in gallium and the lower ones, in molybdenum. But in weightlessness gallium and molybdenum are "equal" and the alloy is a homogeneous composition.

It is quite probable that gallium will provide science with an explanation as to why the Sun emits light. Incredible as it may seem, so far we have had nothing but conjectures about the nature of the colossal energy the Sun has been generating for thousands of millions of years. One of the more widely accepted and seemingly more authentic hypotheses asserts that this is the result of the unceasing processes of thermonuclear synthesis taking place in the Sun's interior. But how is this to be proved?

Neutrinos, the particles produced during thermonuclear reactions could serve as the most convincing, even if indirect, proof. But this piece of evidence is too elusive to get hold of easily. Even Wolfgang Pauli, the Swiss physicist who theoretically predicted the existence of neutrinos back in 1933, suggested that no one would ever be able to prove their existence experimentally, since they have neither mass nor electric charge.

On the other hand, it is a fact that neutrinos possess certain energy and a tremendous penetrating power. Released from the Sun's nucleus, they easily travel through the bulk of solar matter and rush down to earth (and other celestial objects, naturally) in a huge flux. It is believed that more than 60 000 million neutrinos bombard each square centimetre of the surface every second. But it is practically impossible to record them: they effortlessly pass through any substance as if it were an empty space. Nevertheless, physicists have been able to find some materials in which neutrinos should leave a trace. The nucleus of an atom of chlorine-37, absorbing a neutrino, releases an electron and transforms into an atom of argon with the same atomic mass. But this reaction can be effective only with neutrinos possessing great energy, the ratio of which in the flux coming from the Sun is extremely small (less that one ten-thousandth). Hence, almost sterile conditions are needed to capture the evasive particles.

An attempt to create such conditions was undertaken in the United States a few years ago. In order to safeguard against the influence of other space particles a huge tank containing tetrachloroethylene (a common cleaning fluid) was placed underground at a depth of about one and a half kilometres, in an abandoned gold mine in South Dakota. According to theoretical calculations, every 48 hours three atoms of chlorine-37 were to transform into atoms of argon-37, and it was believed, that two such transformations would be owing to neutrinos and the third owing to other radiations filtering even through one and a half kilometres of the earth crust. Alas, only one atom of argon was

detected every two days which meant that most likely the Sun's messengers had nothing to do with it.

Does this mean that no neutrinos come to earth and the thermonuclear theory of the origin of solar energy is wrong? Soviet physicists do not think the experiment described above is enough reason to refute the concept that the Sun is a gigantic thermonuclear reactor. Apparently, to be successful such experiments require even greater accuracy. Besides, theory asserts that the neutrinos in the flux hitting the Earth possess relatively low energy to register which the chlorine-argon method is simply no good. This is where gallium looks a likely prospect. It seems it can serve as a good target (detector, to use the physical term) for low-energy neutrinos. It is suggested that the nuclei of isotope gallium-71 will readily absorb these particles and transform into the nuclei of germanium-71. Having estimated the number of atoms of germanium-71, scientists will be able to measure the Sun's neutrino flux. True, at present it is only a theory, but a gallium-germanium installation has already been built in the Soviet Union and a deep adit for a neutrino observatory has been sunk in the gorge of the Baksan river (Northern Caucasus). Though the installation will require a few tons of gallium, which is quite expensive, the metal will remain practically intact throughout the experiment. It is probable that several years from now gallium will help to shed light on one of the major problems of modern astrophysics.

Rb

AN EVIL GENIE (RUBIDIUM)

If one is to believe the Bible.— The old rocks of Greenland.— The Himalayas grow younger.— A clock that does not tick.— A find in the spectrum.— A brief outline.— Bunsen evaporates a lake.— A quarter of a century later.— In a prison cell.— Clashing with ice.— Far from the nucleus.— Prospect of a power struggle.— A pleasant job.— On the world market.— Related professions.— The clocks chime on time.— Twenty centuries and one second.— Underground treasure troves.— On the banks of the river Kama.— Who dyed the salt?— In the lagoons of the Black Sea.— Protect your men!

How old is our planet? Unfortunately, no “birth certificate” has been preserved while she herself carefully conceals her age (like any woman no longer young). But where there is a secret there will always be people who will want to guess it. The argument concerning the time our “abode” appeared in the universe has lasted for many centuries now. If one is to believe the Bible, it happened quite recently, some six millennia ago. The modern scientific view, however, is that it is about 4 500 000 million years old.

Some of the supporting evidence is provided by ancient mountain rocks. Until recently the rock species found in the region of Transvaal in South Africa were believed to be the oldest on earth: their age is estimated at around 3 400-3 500 million years. But in 1966 Macgregor, a scientist from New Zealand, discovered some rocks at the mouth of Ameralik Fjord in Greenland which are at least 500 million years older. This fact was established by means of the so-called rubidium-strontium “clock”. What is it?

In early 20th century the great British physicist, Ernest Rutherford, suggested that the age of minerals and rocks could be determined through radioactivity, a phenomenon discovered a few years previously. His point was that the atoms of radioactive chemical elements contained in terrestrial material constantly emit some or other nuclear particles, while themselves transforming into atoms of other elements. Interestingly, the speed of this transformation does not depend either on temperature or on pressure, or on any other factor. But every radioactive substance is characterized by its own half-life period, that is, a period during which exactly one half of the radioactive element decays. With some elements this period lasts a few millionths of a second and with others it takes hundreds of billions of years.

The half-life of one of the “centenarians”, rubidium-87 (its proportion in the world rubidium stock is 28 per cent) is 48 000 million years. While spontaneously releasing electrons this isotope slowly but surely transforms into the stable isotope of strontium with the same atomic mass (87) but not subject to further decay. Since the standard ratio of this isotope to its closest "relatives"— the isotopes 88, 86 and 84— is a known factor, it is not hard to estimate the amount of excess strontium-87 in the given rock, that is, the amount formed as the result of radioactive decay of rubidium-87. And having defined the amount of the source material, it can be established how long the process of transformation had taken, hence, to find out the age of the rock.

While the rubidium and strontium isotopes have enabled scientists to determine the prehistoric age of mountain rocks in Greenland, the same pair of elements has convinced scientists that the planet's tallest mountains, the Himalayas, are much younger than was previously believed. For a long time the general scientific view was that the mountain massifs of Central Asia were formed hundreds of millions of years ago. But comparatively recently the fallacy of the old conception was proved by Japanese scientists who had made a careful study of samples of Himalayan rocks with the help of the rubidium-strontium "clock". Their conclusion was that this region had twice undergone most powerful geological compressions. The first, as the result of which the base structure of the Himalayas had emerged, took place about 450-500 million years ago, and the second, which had given rise to the Earth's tallest mountains, occurred a mere 15 million years ago.

Other methods of rock dating include the radiocarbon, uranium-helium, uranium-lead, potassium-argon and some other methods. It must be noted, however, that for great time scales the rubidium-strontium clock is the best.

Thus, rubidium helps to determine the approximate age of the planet Earth. But how long has it itself been known to man? The answer to this question is unambiguous.

Rubidium was discovered in 1861 by two outstanding German scientists, the chemist Robert Bunsen and physicist Gustav Kirchoff. This event was preceded by their development of the method of spectral analysis in 1859 and the discovery of cesium one year later. Pursuing their spectral examination of minerals further, they noticed two unfamiliar dark red lines in the spectrum of Saxonian lepidolite. That meant the mineral contained a new element. They called it rubidium (Latin *rubidius*, dark red) — almost a namesake of the precious stone ruby. But while the ruby is indeed red, rubidium, like most metals, is of a silvery-white colour. It is very light (lighter than magnesium) and as soft as wax. It is not recommended for hot climates: its melting point is 38.9°C and so, it can melt literally before one's eyes somewhere in the south. To wind up our first brief outline of rubidium we shall mention another of its distinctive features: the vapours of rubidium compounds impart a purple tinge to a burner's flame.

Bunsen was the first to obtain metallic rubidium in 1863. It was really a Herculean labour: the chemist had to evaporate a whole "lake" — more than 40 cubic meters of Schwarzwald mineral water in which the new element had also been detected. But that was only a beginning. From the concentrated water solution the scientist obtained a precipitate of platinichlorides of potassium, cesium and rubidium. His next step was to separate the "inseparable" three. Making use of the higher solubility of the potassium compounds, Bunsen first removed potassium by means of repeated fractional crystallization. Separating cesium and rubidium was even more difficult. Bunsen solved the problem and finally obtained the metal by reducing the acid tartarate of rubidium with carbon black.

Twenty-five years later the well-known Russian chemist Nikolai Beketov suggested that metallic rubidium could be obtained by reducing its hydroxide with aluminium powder. For this process he used an iron cylinder fitted with a gas pipe connected to a glass cooler. The cylinder was heated on a gas burner which set off a turbulent reaction, accompanied by the release of hydrogen and sublimation of rubidium into the cooler. Beketov wrote that "rubidium sublimates slowly, running off like mercury and even retaining its metallic lustre as the result of the fact that during the process the vessel is filled with hydrogen". Today this metal is "mined" mainly from its chloride by the action of metallic calcium in a vacuum under a temperature of 700-800°C.

Difficult as it is to extract pure rubidium from its compounds, it is

perhaps even more so to store it. "Fresh" metal is immediately sealed in tubes made from special glass in which a vacuum is maintained or which are filled with an inert gas. Sometimes its "prison cell" is a metal flask filled with dehydrated kerosene or paraffin oil. It is only on these conditions that one can be sure the product will keep for a long time. Why such severe precautions?

The explanation is the "unruly" nature of the "prisoner". To release it from "custody" is the same as to release an evil genie from his bottle. In the family of metals rubidium is inferior in its reactivity only to its "elder brother", cesium. Once set free, that is, on contact with air, it ignites immediately and burns up with a bright pinkish-purple flame, transforming into a yellow powder — rubidium superoxide. This "fire" must not be extinguished with water: rubidium reacts with it even more violently, even explosively, and to make matters worse, hydrogen dissociated from oxygen also flares up instantaneously. Furthermore, rubidium is absolutely indifferent to the state of the water: it is as aggressive towards ice. Just like a miner's pickhammer, it bores into a layer of ice crystals and it is only infernal frost (below minus 108°C) that can pacify the "brawler". Rubidium hydroxide — the product of the reaction — also hurries to demonstrate its wild temper: placed in a glass container, it soon completely destroys it. Under high temperatures (300°C and above) rubidium itself erodes glass quickly, "shamelessly" ousting silicon from its oxides and silicates. This is why rubidium should be "strait-jacketed" in tubes made from special glass capable of defending itself.

The violent chemical behaviour of rubidium is determined by the structure of its atom. Like in other alkali metals, there is only one valence electron in its outermost shell. It is situated farther from the nucleus than the electrons in the atoms of lithium, sodium or potassium, which is why it is easily absorbed by the atoms of other substances (only the atoms of cesium give up their electrons with greater readiness).

Rubidium gives up its electrons as easily under the action of light. This property, called "photoeffect", characterizes many metals but none of them can compare with rubidium and cesium. Although it is a fact that today cesium, the "king of photoeffect", is used in photocells and other photoelectric devices, it is very likely that in time rubidium will "dethrone" the king: its store in nature is 50 times greater than that of cesium and this fact may benefit rubidium sooner or later. Besides, some of its alloys (with tellurium, for one) are characterized by maximum photosensitivity in the far ultraviolet region of the spectrum compared with analogous cesium alloys. In some cases this fact is of primary significance when a material for photocathodes has to be chosen.

Another important area of application of rubidium is organic chemistry where the salts of this metal are used as catalysts. In this role rubidium carbonate was even used more than fifty years ago in the production of synthetic oil. Today it is indispensable in the synthesis of methanol and higher alcohols, as well as of styrene and butadiene — the source materials for the production of synthetic rubber. Relatively recently rubidium catalysts were developed for hydrogenation, dehydrogenation, polymerization and some other reactions of organic synthesis. It is an important fact that such catalysts allow for the reaction to take place under a lower temperature and pressure than with catalysts of sodium or potassium compounds. Another advantage of rubidium catalysts is that they are indifferent to sulphur, the scourge of many catalysts.

American chemists have established that the tartarate of rubidium has a catalytic effect on the oxidation of carbon black, substantially lowering the reaction temperature. "Big deal!" some may think at this point. But scientists, who are now searching for new types of aviation fuel, hold a different view, and most likely, they have good reasons for it.

Some rubidium compounds possess semiconductor properties, others, piezoelectric. But right now these properties are only beginning to interest scientists and engineers.

You have probably noticed that so far we have been talking mostly of rubidium's potentialities rather than its concrete applications in modern technology. And really it has no right yet to claim the role of great toiler like iron, aluminium, copper or titanium. This is illustrated by its production: if the yearly output of all rubidium-producing countries is "scraped together" it will come to just a few dozen kilograms. Hence, its very high price on the international market.

Apart from the fields of application we have mentioned, small amounts of rubidium compounds are used in analytical chemistry as manganese, zirconium and noble metals reagents. In medicine they are found in sleeping drugs and sedatives, and also in preparations used for the treatment of epilepsy. Rubidium salts are components of special optical materials transparent to infrared rays; it is important in the manufacture of luminescent lamps, picture and other cathode-ray tubes. In some types of vacuum devices rubidium plays the role of getter, and in magnitometers and in time and frequency standards, the role of the so-called active substance.

Not long ago a West German electrical engineering firm designed a rubidium device to control the work of ancient clocks that adorn old towers in many European cities. Much admired for their melodious chimes, these clumsy medieval mechanisms are rather unreliable as timepieces. The new device — an atomic frequency standard — guarantees them "clockwork" precision (up to several hundredths of a second in 24 hours).

Still greater accuracy is required in nuclear physics, laser engineering and space navigation where in certain cases chronometric deviations must not be above a few millionths of a second in 24 hours. This is taken care of by an atomic clock designed in the Soviet Union which works on an isotope of rubidium. The underlying theoretical principle is that the atoms of a chemical element can absorb or radiate energy only of a definite frequency which is a constant value for every element, depending only on this element's atomic structure. Therefore, an atomic (or quantum) clock is by several orders more accurate than any other, even the quartz-crystal one, in which the role of the pendulum is played by the elastic vibrations of a quartz plate. The exactness of this clock is such that had it been set at the break of the first century AD, by now it would have been faster or slower by not more than one second.

It can be stated with certainty that in the coming years the applications of rubidium will have extended substantially, which means that its production will also have to increase. The natural reserves of rubidium are adequate, surpassing those of chromium, zinc, nickel, copper and lead.

True, certain difficulties stem from the fact that it is a trace element: although found in many mountain rocks, rubidium has no minerals of its own, let alone big deposits. Ordinarily rubidium associates with the more widely spread alkali metals and is simply inseparable from potassium. Apart from lepidolite mentioned earlier, it occurs in minute quantities (from hundredths to tenths of one per cent) in carnallite from which it is extracted along with other elements. Since the reserves of carnallite are practically inexhaustible, this mineral is believed to be the more promising source material for extraction of rubidium.

Back in the 15th century, in the thick of the Ural forests there emerged the town of Sol Kamskaya (salt of the river Kama), today Solikamsk, a major centre of the chemical industry. This is the region of the richest deposits of carnallites, sylvinites and other potassium salts. Sylvinite looks like marble and occurs in many colours: snow white or iridescent, exhibiting a play of colours from light pink to red, or from pale to almost indigo blue. This mineral (potassium chloride) is interspersed with colourless transparent crystals of sodium chloride (table salt) which sometimes also occurs in pitch black cubes. Why did table salt become black? It is believed that the black crystals are a "visiting card" of rubidium-87, the radioactive isotope which had at one time irradiated sodium chloride.

Rubidium salts are present in solution in the water of the oceans, seas and lakes. Considerable amounts of them are dissolved in the water of the famous Odessa lagoon on the Black Sea, but their concentrations are even higher in the Caspian sea. Traces of rubidium are found in many plant species, in seaweed, tobacco, tea leaf and coffee beans, in sugar cane and beet root, grapes and some citrus fruits.

We are going to wind up our story about rubidium with a joke. A few years ago the most successful newspaper article was one entitled "Protect Your Men!". Now according to the Great Soviet Encyclopaedia, we must indeed not only protect but treasure them: their blood contains more rubidium than the blood of women (0.00032 and 0.00028 per cent respectively).

Sr

THE SECRET OF THE BENGAL PRIESTS (STRONTIUM)

Why were the Cossaks ill?— A village that went down into history.— Hurry up with your conclusions!— The Bengal priests' patent.— Lights in the sky.— A "sweet" job.— The many jobs of strontium.— An explosion over Bikini.— A dangerous virus.— Good prospects.— Strontium gets into the clock.— Working on a remote Northern island.— The Tristan submerges.— A magic generator.— Small jobs.— Without a spark.— Blue crystals.— In the coastal shallows.— In days gone by.— Nature is in no hurry.

In late last century the Cossaks of the Trans-Baikal area in Siberia moved to the region of the Urov, a tributary of the river Argun, where there was good ploughland and a fair climate. But misfortune awaited them: a few years later many settlers had contracted a mysterious disease that struck people down and twisted their bodies with pain. Doctors arrived many times but none was able to establish the cause of the malady. It was only in our day that the combined biological, geological and chemical expeditions of the USSR Academy of Science found that the disease-carrying agent was strontium, considerable amounts of which were contained in the local water.

What is this treacherous chemical element that gave such a hostile reception to the newcomers?

Strontium was discovered at the end of the 18th century and it owes its name to Strontian, a small village in Scotland (it would be more appropriate to say that owing to this element an obscure village went down into the history of chemistry). It all started in 1787 when a rare mineral was unearthed not far from the village and was given the name strontianite. Among the scientists who became interested in the mineral were the British chemists Crawford and Hope, and the German chemist Klaproth. Their studies indicated that the new mineral contained the "earth" (oxide) of an unknown metal.

Soon there was a new development: in 1792 Hope produced convincing proof that this was indeed a new element. It was given the name strontium (in the Russian literature of the beginning of the 19th century we come across other names: strontiy, strontian and strontiyan).

T. Lowitz, a Russian chemist, could probably also be considered one of the first discoverers of strontium. In the same year, 1792, he detected a "strontian earth" in the mineral barytes, but being extremely accurate, he decided to act on the principle "look before you leap" and started a new series of experiments to make absolutely sure before announcing his findings. When he was through and was ready to publish his article *On Strontian Earth in Heavy Spar* it was too late to "leap": the chemical journals reporting the results of the studies by Hope, Klaproth and other scientists had reached Russia. It seems, folk wisdom is not always so good after all.

Scientists were able to see pure strontium for the first time a few years later, in 1808, when Sir H. Davy of Britain succeeded in isolating this light (lighter than aluminium), silvery metal. But man's acquaintance with the chemical compounds of strontium had begun long before that.

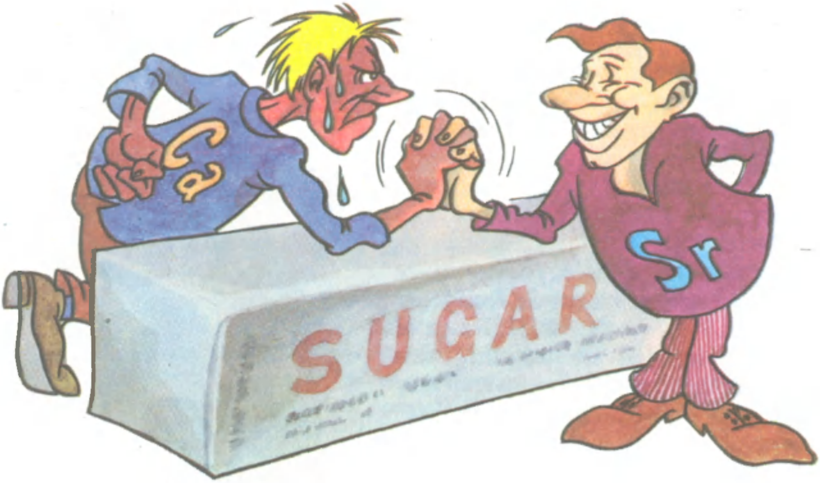
Records from ancient India refer to mysterious red lights that sometimes flared up in dark temples and put terror into worshippers. The omnipotent Buddha, naturally, had nothing to do with it. It was his true servants that had — the priests, who rubbed their hands delighted to see the awe-stricken faces of their flock. To achieve this effect they mixed strontium salts with coal, sulphur and Berthollet's salt, pressed the mixture into small balls or cones and quietly set fire to them when they wanted it. It is likely the Bengal priests held the "patent" to the mixture since the name "Bengal light" has been in common use since time immemorial.

The property of the volatile compounds of strontium to burn with a brilliant red glow has been used in fireworks for ages. For example, in Russia under Peter I and Catherine II not a single more or less important occasion passed without what was called "mock fires". In our day too, the displays of red, green and yellow lights in the evening sky on holidays owe much of their brilliance to strontium.

But it is not only during amusements that the pyrotechnical skills of the "metal of red light" are indispensable: it is hard to say how many lives were saved in seas and oceans, owing to the signal flares fired from ships in distress to show the way to rescue boats.

To give red light remained the only use of strontium for a long time. Then, at the turn of the century, chemists discovered it was good for sugar refining, as it considerably increased the extraction of sugar from molasses. A few years later, however, strontium had to give up its "sweet job" to the cheaper calcium. But curiously enough, of late the question of resurrecting the strontium method has been given serious consideration, for it will ensure a 20-per-cent increase in sugar extraction.

We could list several fields where strontium has been used more or less successfully. In metallurgy it helped to purify steel from gases and



harmful impurities; in the making of glazes it replaced the poisonous compounds of lead, an element which is not even abundant enough; in glass-making its oxide was used instead of some expensive materials going into the manufacture of glass fibre and various special purpose glasses. The synthetic crystals of strontium titanate can easily compete with diamonds in the play of light and lustre displayed by its facets. The presence of strontium in portland cement increases its moisture resistance which is of especial significance in the building of hydraulic structures. In electronics strontium is applied for oxidizing the cathodes of electron tubes and as a getter (a gas absorbing material), particularly for dielectrics and ferroelectrics. Strontium compounds are included in the composition of phosphors and very stable house paints and greases. The isotopes of rubidium and strontium enable scientists to establish the age of prehistoric mountain rocks with considerable accuracy (more on this in the previous chapter).

Thus, it seems there is enough work for element No. 38. Nevertheless, everything described above should be regarded as isolated episodes in the history of strontium. Before going over to the most important aspect of its activity, let us recall one event of recent history which was the focus of attention of the world press for a long time.

In March 1954 a gigantic mushroom-shaped cloud rose over Bikini atoll in South Pacific, announcing the explosion of an American hydrogen bomb. A few hours later greyish-white flakes of radioactive fallout began to drop on board a Japanese fishing vessel which was in the open sea, about 150 kilometres from the epicentre. The fishermen stopped work and set course for home. But it was too late: soon after their arrival one of the men was dead and the rest were suffering from a severe form of radiation sickness. Strontium-90, one of the numerous radioactive isotopes formed during the process of radioactive decay, was probably the main “virus” of the disease.

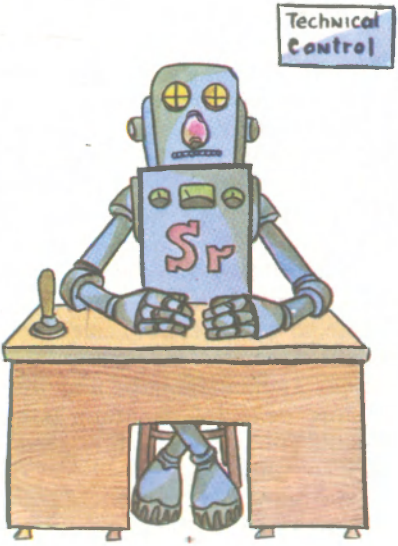
An explosion like the one at Bikini sends into the sky tens of millions of tons of earth and rocks literally stuffed with products of nuclear fission, the most toxic, hence most dangerous, of which is strontium-90. Sooner or later these products settle on the surface of oceans and continents, where human beings are easy prey to it: through fruits and vegetables they get it from the soil, from drinking water and from the meat and milk of animals grazing on grass contaminated with strontium-90. Accumulating in the human organism it creates dangerous radioactive seats that have a lethal effect on the bone tissue and marrow and on the blood.

Progressive mankind have spared no effort to achieve a complete ban on atomic and hydrogen bomb tests. Millions of people acclaimed the international agreement banning nuclear tests in the atmosphere, outer space and under water signed in Moscow in 1963. However, this does not mean that radioactive strontium is to disappear from the sphere of human activity: the development of nuclear power creates vast possibilities for its peaceful uses in science and engineering. This is where its applications may be limitless.

One of the more promising fields is the application of radioactive strontium in nuclear batteries on board space rockets and artificial earth satellites. These batteries are based on the ability of strontium-90 to radiate electrons of great energy which is converted into electricity. Radioactive strontium cells in a battery not larger than a match box serve without recharging for 15 to 25 years.

Nuclear batteries will doubtlessly find application in telephony and radio engineering. In the meantime, Swiss watch-makers have successfully installed tiny strontium batteries in electric clocks and watches.

The simple and practically inexhaustible sources of electric power are indispensable at automatic meteorological stations in deserts, polar regions and mountains. In Canada on a remote northern island in a spot difficult of access an atomic meteorological station has been installed for unattended operation for a period of two or three years. The energy source for the equipment is radioactive strontium (400 grams only) encased in a special three-layer alloy and protected by a lead screen. The entire equipment is housed in a steel cylinder 2.5 metres high, 0.65 metre in diameter and weighing about one ton.



An interesting development is the *Tristan* strontium thermoelectric battery designed by the West German firm Siemens and intended for deep water research apparatus. Though not large in size, the battery weighs 1.4 tons owing to its thick lead shield: a reliable protection for people and marine animals from radiation, the level of which near the battery is only a fifth of the permissible value.

Another strontium generator for automatic meteorological stations has been designed in the Soviet Union. *Beta-C*, as it is called, has a guaranteed service life of ten years. All its maintenance needs is a preventive inspection once in two years. This battery won a gold prize at the Leipzig Fair. The first such generators have been installed at meteorological stations in the Transbaikal area and in the upper reaches of the river Kruchina in the Siberian taiga.

The number of instruments operating on radioactive strontium grows every day. Among them are thickness gauges used in industries producing paper, fabrics, metal strip, plastic film, paints and varnishes, and also gauges measuring density, viscosity, etc., as well as in flaw detectors, radiation monitors and various signal devices.

The atomic beacon *Tallin*, seen like a red candle shining over the sea at the entrance to Tallin port on the Baltic Sea, also operates on strontium generators, converting heat into light. It is noteworthy that no "lighthouse keeper" tends the *Tallin*: its equipment is inspected several times a year by specialists and that is all.

Often at engineering plants one comes across beta-relays installed to control the delivery of blanks to be machined, the correctness of their position, the serviceability of tools, and other such "small jobs". The principle of operation of the relay is simple. A microcharge of strontium, radiating on a level 200 times below the sanitary norm, is encased in a lead flask that has a tiny window transparent to beta-radiation (electron flux). As long as a blank or tool remains within the "field of vision" of the beta-rays, that is, as long as everything is in order the relay is inactive. But if, say, a drill breaks and drops out of "view", the radiation flux directly hits the gas alarm and the relay operates, stopping the machinery and switching on the signal light on the dispatcher's panel to indicate the place of the break-down.

The electric charges of up to several thousand volts caused by friction in the production of paper, fabrics, synthetic fibres, plastics, etc., create the danger of a spark puncture and fire. Until recently such emergencies were taken care of by extremely complex, bulky and expensive devices ionizing the air by means of ultraviolet or X-rays. At present they have been replaced by strontium ionizers, which are not expensive and do not require high-voltage installations. They are simple to operate, compact and durable. The new device has made it possible to increase the productivity of looms several times over, sharply reduce spoilage and idling caused by breakage of the thread.

Thus, peaceful strontium is making its sure way in industry and the demand for it is constantly growing. Will nature be able to meet all the need for this metal?

Strontium-containing minerals are scarce. It is only strontianite and celestine that sometimes occur in sizable accumulations. This is how

the outstanding Soviet geochemist and mineralogist, Academician Fersmann described celestine: "... In a fresh break of rock I suddenly saw a blue crystal. Oh, that was real celestine! A wonderful, transparent blue needle like the clear sapphire of Ceylon, like a delicate, sun-bleached cornflower".

Blue is not the only colour of celestine: at times pale-violet, pinkish or smoky-black crystals are found in mountain rock cavities. Exceptionally beautiful are amber-and yellow-coloured druses of sulphur studded with its greenish crystals.

In nature celestine is formed in different ways. One of them was described by Academician Fersmann, whom we quote once more:

"...At the dawn of Time, several tens of millions of years ago, the waves of the Upper Jurassic sea were rolling down as far as the mighty ranges of the Caucasus, already then rising steeply over the water...

"In the coastal shallows, on the stones, there lived countless tiny radiolaria. They were sitting on stones, on beautiful colonies of pearlwort, or even on the needles of sea-urchins with whom they travelled along the seabed. Those were the famous radiolaria-acantharia, whose skeletons consisted of minute spicules, from 18 to 32 in number. In the course of their complicated life process the numerous radiolaria had been accumulating the salt of strontium sulphate, extracting it from sea water and gradually building their crystalline spicules.

"Dead radiolaria fell to the sea bottom and accumulations of strontium sulphate grew. Thus began the history of a rare metal..."

It is only to be added that there were other marine species that extracted celestine from sea water: scientists found spiral shells of prehistoric molluscs composed of celestine. Some of them were 40 centimetres in diameter.

Sizable volcanogenic and sedimentary deposits of strontium are found, among other places, in the deserts of California and Arizona (USA). (As a matter of fact, it has been noticed that strontium "likes" hot climates and occurs in northern parts far less frequently.) In the

Tertiary Period this region was the scene of violent volcanic activity. The thermal waters that burst forth with the lava from the depths of the earth were rich in strontium. The lakes situated amidst the volcanoes had been accumulating it and creating considerable stores over millennia.

Strontium is also contained in the water of Kara-Bogaz-Gol on the Caspian Sea. There the continuous process of evaporation constantly increases the concentration of salts. When saturation point is reached they form a precipitate which occasionally contains as much as one or two per cent of strontium.

Several years ago geologists discovered a fairly large deposit of celestine in the mountains of Turkmenia (Soviet Central Asia). The blue veins of this valuable mineral are deposited on the slopes of gorges and deep canyons of Kushtangtau, a mountain range in the south-western part of Pamiro-Alay. The "celestial" stone from Turkmenia is expected to do much good to our national economy.

... Nature is not disposed to haste: it began creating the strontium reserves we find today millions of years ago. But as in those days, the complicated chemical processes continue and a new treasure is accumulated in the depths of the earth, beneath the waters of seas and oceans. This will be nature's gift to the generations to come.

Y

A FIND IN AN OLD QUARRY (YTTRIUM)

Arrhenius's hour of triumph.— A mysterious earth.— Years of plenty.— Why the earth became yellow.— A new page in a biography.— Emerging from concealment.— In order of priority.— Mosander's "trio".— Rare-earth "fever".— Aldebaranium and Co.—15 000 crystallizations.— Almost namesakes.—"Housing problem."— What came to light after two centuries.— The lamp is ignited by a match.—"Windows" of rockets.— Progress in colour television.— A "vitamin" for cast iron.— Are rare-earth elements rare?— In honour of Yuri Gagarin.

In 1787 Karl Arrhenius, a lieutenant of the Swedish army, decided to spend his holidays in Ytterby, a village on one of the numerous islands near the Swedish capital Stockholm. His choice was not accidental: an ardent amateur mineralogist, he knew that near Ytterby there was an exhausted and long-abandoned quarry where he hoped to replenish his collection of minerals. Arrhenius spent day after day, carefully studying new areas of the quarry, but for a long time he had nothing to show for it. Finally he was rewarded when he unearthed a heavy black stone which looked like common coal. He could not tell what it was and that was a good sign. Arrhenius was beside himself with joy, although he could not foresee that his unsightly mineral was to play a major role in the history of inorganic chemistry and would sign the name of its first discoverer in its history.

Arrhenius's holiday had come to an end, and returning home, he put down a description of the black mineral, which without much further ado, he called ytterbite in honour of Ytterby, and resumed his military service. From time to time he returned to his mineralogical searches, but his hour of triumph had already passed.

In 1794 ytterbite drew the attention of the Finnish chemist, Professor Gadolin of Abo (now Turku) University. To him, a prominent scientist, the black stone from Ytterby brought luck and to a large extent determined the future career. It will be noted in passing, that in 1811 he was elected corresponding member of the St. Petersburg Academy of Sciences. Gadolin analyzed the element chemically and discovered that along with the oxides of iron, calcium, magnesium and silicon, it contained a considerable amount (38 per cent) of an unknown substance, some properties of which resembled aluminium oxide and some calcium oxide. The scientist surmised that it was the oxide of a new chemical element, or a new "earth" as the high-melting oxides of some insoluble elements were referred to in those days.

Three years later the study of ytterbite was taken up by the Swedish chemist Anders Ekeberg, Professor of Uppsala University. He confirmed his Finnish colleague's conclusion, but was inclined to think that the content of the new element in the rock was not 38 but 55.5 per cent. He suggested that the mysterious earth should be called yttrium and that ytterbite should be renamed gadolinite as a token of respect for Gadolin, the first student of the mineral, and in recognition of his great services to science.

The interest in yttrium earth was growing by the hour among the scientific circles. Numerous studies conducted in different countries confirmed that gadolinite indeed contained a new element. However, the quantitative characteristics of it offered by the studies were widely different: none of the chemists "furrowing" yttrium earth far and wide suspected that it concealed not one but several oxides of unknown elements.

Cerium earth, discovered in 1803, appeared to be as complex in composition. As transpired later, the two earths "housed" almost all the elements in the Mendeleyev Table from No. 57 through 71 and called lanthanides, which, together with their close "relatives" scandium (No. 21) and yttrium (No. 39), make up the family of rare-earth metals. But a whole century was needed for scientists to break up yttrium and cerium earths into their component parts and discover all the elements they contained.

The beginning of the 19th century was marked by the discovery of a large number of new elements, including palladium, rhodium, osmium, iridium, potassium, sodium, barium, strontium, calcium, magnesium, lithium and cadmium. Those and other "newborn" elements attracted the attention of chemists and the interest in yttrium and cerium earths had dampened noticeably.

It is likely that the famous Swedish chemist Berzelius and his pupils alone were still preoccupied with the rare earths. In 1818 Scherer, one of Berzelius' assistants, discovered that when heated in a sealed vessel yttrium earth, normally a colourless powder, acquired a strange yellow tinge, which disappeared only after the process was repeated in a reducing atmosphere. Scherer concluded that along with yttrium the substance contained an unknown oxide which was responsible for the yellow "complexion" of the earth. Similar views had been expressed before, but no further progress had ever been made. Neither was Scherer able to confirm his idea experimentally.

Several years had passed and in 1828 a new page was turned in the biography of yttrium: Friedrich Woehler (another of Berzelius' pupils) extracted metallic yttrium. Though the metal was full of impurities, the event was regarded as a breakthrough, since the separation of any of the rare-earth elements from the chemical compounds containing them is an extremely difficult job even today.

The next page in the history of yttrium, or to be more precise, of all the rare-earth elements (their lives are most intimately connected), was turned by yet another pupil of Berzelius, the talented Swedish chemist, Karl Mosander. In 1826 he became seriously interested in cerium earth and found that just as yttrium earth, it was likely to contain an unknown oxide. But Mosander was not in the habit of making hasty categoric statements, especially since he had failed to isolate the new earth. He was by then distracted from his study of cerium oxides by other things and it was only at the end of the 1830s that he resumed it.

He repeated his previous experiments with cerium earth and was now able to prove that it really contained an oxide of another element. On Berzelius' suggestion he called it lanthanum (concealed, in Greek). Indeed, lanthanum had spent a long time in concealment behind cerium's back, but to make up for it, it later showed exceptional hospitality, letting its home to all of its rare-earth relatives and giving them the right to be called lanthanides.

But apart from the oxide of lanthanum, Mosander discovered another substance in cerium earth. Later it was found that it also had a complex composition, and finally, several rare-earth elements were extracted from it. Now came the turn of yttrium earth. Mosander remembered about its "yellow days" in Scherer's experiments, neither did he forget that the figures for the content of yttrium oxide in gadolinite differed considerably in the experiments of Gadolin, Ekeberg and many other researchers, despite the similar methods of analysis they had employed. Here was a problem that would take much brain-racking, especially if one considered that Berzelius himself had been unable to explain the differences convincingly.

But where should he begin? First of all, Mosander tried to obtain a specimen of yttrium oxide as pure as possible. He was not content with the methods science knew then and developed new ones especially for his experiments. Subsequently they were accepted as basic ones for the chemistry of rare-earth elements. In order to "split" yttrium earth, Mosander used fractional precipitation based on the slight difference in the solubility of the salts of rare-earth elements in acids. If one was to assume that yttrium earth was a mixture of oxides, they would precipitate not all together, but each in its turn.

Days stretched into weeks and months. The scientist kept adding, literally by the drop, the oxalate of patassium, ammonia and other reagents to yttrium hydrate. One painstaking experiment was followed by another, and finally, in October 1843, Mosander published the results of his experiments. It appeared that yttrium earth contained three oxides: in the process of fractional precipitation Mosander had first obtained a yellow deposit, then a pinkish one, and lastly, one that was colourless. The names Mosander gave his oxides and their respective elements symbolized, as it were, the splitting of the base earth contained in the mineral from Ytterby: the colourless oxide was called yttrium (the first three letters of the village's name), the yellow, terbium (middle of the name) and the pinkish, erbium (middle and end of the name).

But it was still too early to consider the question closed: a lively polemics flared up around Mosander's "trio" in which many leading chemists took part. Some doubted the existence of the newly discovered earths, others insisted that the earths should be divided into independent "territories" belonging to yet unknown elements. The truth, however, lay somewhere between those two extremes: erbium earth indeed turned out to be a mixture of oxides. In 1878 the Swiss chemist Marignac split it into erbium and ytterbium. But it was soon found that each was also a mixture of oxides...

The fractionalization of the earths continued and the family of lanthanides was growing and with it grew the interest in rare earths. A great contributing factor was the method of spectral analysis developed by Robert Bunsen and Gustav Kirchhoff of Germany and offering infinitely broader possibilities of unravelling the mysteries of matter.

Just as in the times of the gold rush when thousands of adventurers flocked to California and Klondike, the last quarter of the 19th century saw numerous scientists headed for the shores of the Rare-Earth

Archipelago in search of chemical treasures. It seemed there would be no end to discoveries of new rare-earth elements (there were more than one hundred in all). Unfortunately, few of them possessed adequate characteristics to be given a permanent place in the periodic table. But the "newborns" were given beautiful names by their lucky "parents": philippium and decipium, demonium and metacerium, damarium and lutium, cosmium and neocosmium, glaucodidymium and victorium, euxenium and carolinium, incognitum and cassiopeium and even aldebaranium... Today these resounding names can be found only in the lists of false discoveries.

But there was also some good luck. Apart from erbium proper, erbium earth yielded thulium, holmium and dysprosium, and ytterbium earth, besides, ytterbium produced scandium and lutecium. It is noteworthy that in order to isolate lutecium the French chemist Georges Urbain had to carry out more than 15 000 crystallizations — this is how unwillingly nature gives up its secrets. Lutecium was the last rare-earth element discovered (1907), and by a curious coincidence, it took the last place in the lanthanide row.

Thus, all the rare-earth elements were finally discovered. Let us sum up some of the results. A small Swedish village where Arrhenius had once found a black stone gave names to four chemical elements — yttrium, terbium, erbium and ytterbium. Not a single continent, state or national capital had ever been accorded such honour. The black mineral gadolinite (ytterbite) was also a champion of a kind: it was found to be a storage of a dozen or so new elements.

It must be said that yttrium and other rare-earth metals were quite a problem for Mendeleyev when he was accommodating them in his table of elements. At the time of discovery of the periodic law science knew only six rare-earth elements and to find a place for each of them was extremely difficult because of their amazing chemical similarity. As the number of such elements grew, the "housing problem" was becom-

ing even more acute. More than one decade had passed before it could be settled. As a result, yttrium which had begun the history of rare earths had to be given a separate "apartment". Scandium was given the same privilege. As for the rest of the rare-earth elements, they had to be placed in a "communal flat" with lanthanum as the host. Though some of the lanthanides belong to the yttrium group (the rest to the cerium one) yttrium was dissociated from them in the elements table.

Almost two hundred years have passed since the time yttrium was discovered. It would seem the time was adequate to study this element in every detail. However, the information on its density, melting and boiling points and some other characteristics are not identical in different reference books. This is to be explained by the fact that the metal obtained by different researchers differs in purity. Today 99.8-99.9 per cent pure yttrium can be obtained by melting in a vacuum followed by two- or three-time distillation. This metal melts at 1 500° C and its density is 4.47 g/cm^3. The combination of a comparatively high melting point with small density and fair strength characteristics, as well as some other valuable properties promise yttrium a good future as a structural material. It has already been tried out in pipes for transporting liquid nuclear fuel — molten uranium or plutonium. But right now it is being more extensively used in other fields.

As early as the end of the last century, marked by a boom in the development of electricity, the German physicist Walter Nernst invented an incandescent lamp, in which the standard carbon or metal filament placed in a vacuum or an inert gas was replaced by an exposed rod prepared from a mixture of the oxides of zirconium and yttrium. His idea was that some crystalline compounds, the so-called solid electrolytes, conducted electricity as a result of the movement of ions and not electrons. The Nernst lamp had to be ignited by a match, since the rod began to conduct electricity only heated to 800° C. That was why at that time the lamp was not widely used, but today heating elements of this kind are extensively applied in technology to create high temperatures (with the oxide of yttrium being substituted by that of calcium). Unlike its metal counterparts, such heaters are not oxidized in the air, but on the contrary, work the better the higher the oxidizing properties of the medium.

Today a high-purity oxide of yttrium is the basis for the production of yttrium ferrites used in radio electronics, in hearing aids and in computer memory cells. The borides, sulphides and oxides of yttrium are used in the cathodes of powerful generators and refractory crucibles for high-melting metals. One of the developments of the last few years is zyttrite, a new refractory material consisting of zirconium ceramics with additions of yttrium, characterized by minimal heat conduction and by an ability to retain its properties up to 2 200°C. Another new ceramic material — yttrilox — melts at 2 204°C. It consists of the solid solution of thorium dioxide in yttrium oxide and is transparent like glass in the visible band of the spectrum, while at the same time readily transmitting infrared radiation. It can be used to make infrared "windows" in various devices and rockets and peep-holes in high-temperature furnaces.

Yttrium has made an important contribution to the development of colour television: the picture tubes with red phosphors based on its compounds produce an extra bright glow. In Japan this purpose is served by yttrium oxide activated by europium; in other countries the orthovanadate of yttrium is preferred. According to Japanese estimates, it takes something like 5 tons of pure yttrium oxide to make one million tubes.

But perhaps it will be no exaggeration to say that at present metallurgy is the most important field of application of yttrium. Every year this metal is being increasingly used as an addition in the production of alloyed steel and inoculated cast iron. The introduction of small quantities of yttrium in steel makes it fine-grained and improves its mechanical, electric and magnetic properties. If a little yttrium (tenths or even hundredths of a per cent) is added to cast iron its hardness grows almost twice and its wear-resistance, four times. Furthermore, this metal is less brittle and approximates steel in its strength characteristics and better resists high temperatures. An important point: yttrium iron can be remelted several times, with "vitamin Y" retaining all its fine properties.

Yttrium improves the heat-resistance of nickel-, chromium-, iron- and molybdenum-based alloys, increases the ductility of the high-melting vanadium, tantalum, tungsten and their alloys and considerably strengthens titanium, copper, magnesium and aluminium alloys. The light magnesium-yttrium alloy (9 per cent of yttrium) possessing high corrosion-resistance is used in the manufacture of some parts and units of flying vehicles.

Yttrium is commercially produced both in its pure form (single crystals and ingots) and alloyed with magnesium and aluminium.

Its production is constantly expanding. Only recently the entire world output of it was measured in kilograms and today world yttrium consumption is over one hundred tons a year. Is it so rare after all?

Apparently it is not. Not only yttrium but most other rare-earth elements occur in nature sufficiently frequently. The content of yttrium in the earth's crust is 0.0029 per cent, which means that it is one of the 30 most widespread elements on the planet. The reserves of this element are tens of times greater than those of, say, molybdenum or tungsten, hundreds of times greater than the reserves of silver or mercury and thousands of times greater than the reserves of gold or platinum. Perhaps it would be more appropriate to treat the term "rare-earth elements" as a survival from the history of their discovery and not as a true estimation of their distribution in nature.

Yttrium is contained in over a hundred minerals. They include yttrium minerals proper, such as xenotime, fergusonite, euxenite and thelenite. In 1961 Soviet scientists discovered accumulations of a hitherto unknown yttrium-containing mineral in Kazakhstan. It was named gagarinite in honour of the world's first spaceman. Its discoverers gave one of the best samples of the mineral to Yuri Gagarin. A beautiful druse of gagarinite — large pale-yellow hexahedral crystals — is on display in the Fersmann Mineralogical Museum of the USSR Academy of Sciences.

Tc

DINOSAUR RESURRECTED (TECHNETIUM)

Is yesterday coming back?— One good turn deserves another.— Damaged reputation.— Hard luck.— Was it a waste of time and effort?— "Categorically forbidden!"— Impertinent neighbours.— A short life.— Missing.— Developments in artillery.— A visit overseas.— Better less than nothing.— Without further ado.— Miraculous splinters.— Could it be had cheaper?— Not a tasty dish.— An impregnable fortress.— Near zero.— In the constellation Andromeda.— Abandoned theories.— Dinosauri take a stroll. .

Imagine coming across a staggering piece of news like this in a paper one fine morning:

> *Newborn Dinosaur*
>
> *Success was reported yesterday from the zoo of the city N. where scientists have spent years interbreeding a crocodile with a kangaroo in an attempt to resurrect the dinosaur, the animal that had roamed our planet in the Mesozoic era and died out many millions years ago.*

You realize, of course, that such an item could be published only on All Fools' Day. There is no setting the clock of history centuries back and returning the past.

Although it is true that scientists cannot resurrect the dinosauri or pterodactyls, sometimes they manage to achieve no less astonishing results in other fields. Here we are referring to the "resurrection" of some chemical elements that "inhabited" the Earth at one time but had gradually completely disappeared owing to radioactive decay. The first such element was technetium obtained in 1937. But before going into that let us make a digression into the history of chemistry.

Back in 1846 R. Hermann, a chemist and mineralogist working in Russia, came across an unknown element in the Ilmen mountains in the Urals and named it yttroilmenite. He did not leave the matter there and tried to extract the new chemical element he believed the mineral contained. No sooner had he discovered his ilmenium, than the well-known German chemist H. Rose refuted the discovery and proved the fallacy of Hermann's work. (Hermann was soon able to take his revenge: when Rose announced his discovery of pelopium, Hermann did his best to disprove him and succeeded.)

A quarter of a century later ilmenium was back on the chemical scene: it was remembered as pretender to the role of eka-manganese which was to take the vacant square 43 in the elements table. But ilmenium's reputation had been greatly damaged by Rose's work and despite the fact that many of its properties, including the atomic weight, appeared to fit those of element No.43, Mendeleyev refrained from placing it in his table. Subsequent research irrevocably proved that ilmenium would remain in the history of chemistry only as one the ill-fated pseudo-elements.

But since a vacancy must always be filled, pretenders to No.43 began to grow like mushrooms. Davium, litium, nipponium — all burst like soap-bubbles almost the minute they were discovered.

Finally, in 1925 Ida and Walter Noddack of Germany published their paper informing of their discovery of two elements — masurium (No.43) and rhenium (No.75). It was all "smooth sailing" for rhenium: it was immediately "legalized" and placed in the residence prepared for it. As for masurium, luck was not with it: neither its discoverers nor other chemists could furnish scientific evidence of its existence. True, Ida Noddack declared that "soon masurium will be available in shops just like rhenium". But chemists are not known for a trusting lot, and since the Noddacks could produce nothing more convincing than Ida Noddack's declaration, the list of the "pseudo-43rds" had another unfortunate name added to it.

By that time some scientists were beginning to think that not all elements predicted by Mendeleyev, the least so element No.43, existed in nature. Could they be right and the whole to-do around the issue was a waste of time and effort? One of the scientists to "veto" masurium was a German chemist W. Prandtl.

At long last the matter was cleared up by nuclear physics, the younger sister of chemistry that had by then won considerable authority. One of the regularities governing this science is a selection rule observed in the 1920s by the Soviet chemist S. A. Shchukarev and defined by the German physicist H. Mattauch in 1934. But before explaining it, let us recall what are isotopes and isobars. Isotopes are atoms of a chemical element having similarly charged nuclei but different mass numbers. Isobars, or isotopes of equal mass, have differently charged nuclei.

Now back to the selection rule. In substance it means that two stable isobars, the nuclear charges of which differ by one, cannot exist naturally. In other words, if a chemical element has a stable isotope, its immediate neighbours in the elements table are "categorically forbidden" to possess a stable isotope with the same mass number. In this sense, element No.43 was extremely unlucky: its neighbours on the left and right — molybdenum and ruthenium — filled all vacancies in the immediate vicinity with their own isotopes. That meant that element No.43 was in for hard luck: no matter how many isotopes it would have, they would all be destined to be unstable. That was why they were disintegrating day and night.

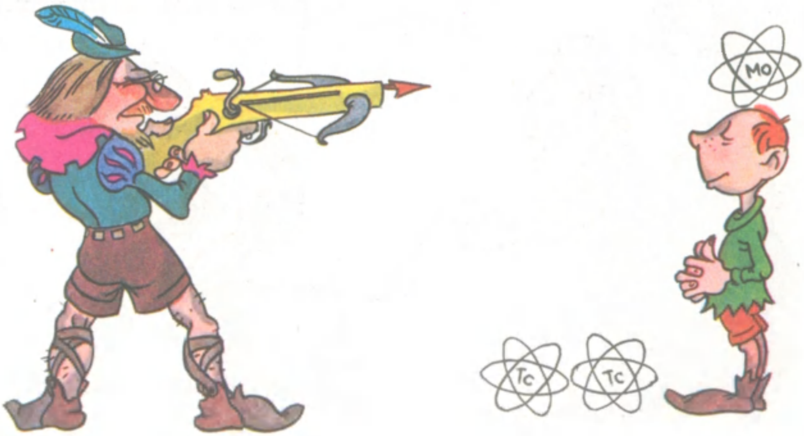
It is reasonable to suppose that element No.43 had existed on the planet in appreciable quantities at one time but had gradually disappeared, owing to the continuous process of radioactive decay. Why then have uranium and thorium survived to our day? They are also radioactive, hence have been disintegrating from the very first day of their life. The answer is that they have survived only because they disintegrate much more slowly than other elements with natural radioactivity (all the same, the reserves of uranium over the period of our planet's existence have diminished to a hundredth part of what they used to be). American radiochemists have found that an unstable isotope of an element has a chance to survive in the earth's crust from the moment of the "creation of the world" to our day only if its half-life is over 150 million years. Now taking a look ahead it must be said that when different isotopes of element No.43 were obtained, it was established that the half-life of the one with the longest life was a little over two and a half million years, which means that the last of its atoms ceased to exist long before the appearance of the first dinosaur, bearing in mind that the age of the planet is estimated at 4.5 thousand million years.

It appears then that if scientists wanted to "touch" element No.43 with their own hands they had to create it also with their own hands, for nature had long included it in the list of those "missing". Could science cope with a task of that magnitude?

Yes, indeed, as was experimentally proved by the outstanding British physicist Ernest Rutherford in 1919. He subjected the nuclei of an atom of nitrogen to a fierce bombardment by alpha-particles formed in the continuous process of nuclear disintegration of the atoms of radium. The result of the prolonged bombardment was that the nuclei of the atoms of nitrogen were "replenished" with protons, while nitrogen transformed into oxygen.

Rutherford's experiments gave science an extraordinary piece of artillery, enabling it not to destroy but transform one element into another and even create new elements.

Could element No.43 be produced in such a way? The problem was tackled by an Italian scientist, Emilio Segrè. At the beginning of

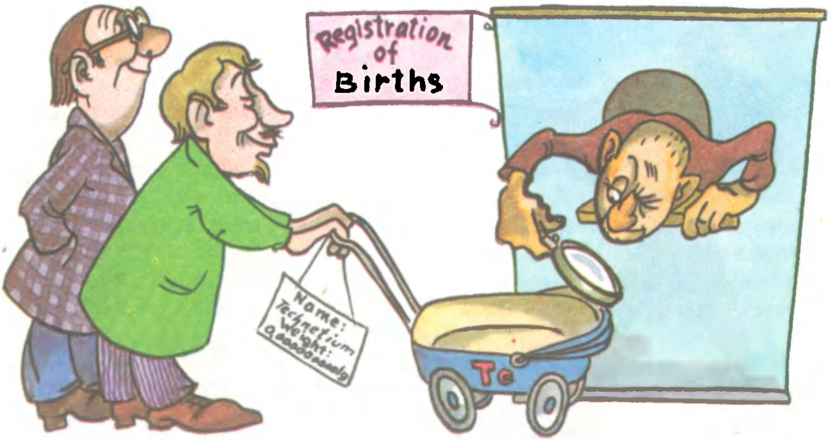


the 1930s he worked at Rome University under the already famous Enrico Fermi. Together with the other "boys" (Fermi's name for his gifted pupils), Segrè took part in Fermi's experiments with the neutron irradiation of uranium, and worked on many other problems of nuclear physics. But the day arrived when Segrè was made an alluring offer — to head the physics chair at Palermo University. On his arrival at the ancient capital of Cicily, however, Segrè was disappointed: the laboratory he was to head was nothing much to look at and could hardly be a source of scientific inspiration.

Segrè's desire to go on with his studies of the atom was great and in the summer of 1936 he crossed the ocean to visit the American town of Berkley. There, in the Radiation Laboratory of California University, the cyclotron — accelerator of atomic particles — invented by Ernest Lawrence, had been in operation for several years. Modern physicists would perhaps find this small installation no more than a child's toy, but in those days the world's first cyclotron was admired and envied by scientists in other laboratories (in 1939 Lawrence was awarded the Nobel Prize for his invention.)

The time for Segrè's departure from the USA had crept up unnoticed. Parting with the cyclotron was hard: Segrè could not even dream of such equipment then. Just before leaving, it occurred to him to take with him one of the molybdenum plates which had for several months been receiving a powerful flux of cyclotron-accelerated deuterons, that is, nuclei of heavy hydrogen (deuterium). Lawrence was glad to help his colleague and Segrè returned to Palermo with a few priceless specimens of molybdenum.

What was Segrè's idea? He wrote later: "We had good reasons to believe that after bombardment with deuterons molybdenum had to transform into element No.43..." Indeed an atom of molybdenum contained 42 protons in its nucleus. If a deuteron, consisting of a proton and neutron, managed to break through to the nucleus of an atom of molybde-



num it would bring the number of protons to 43, that is, exactly to as many as the nucleus of element No.43 should have.

Everything seemed clear-cut as far as theory was concerned, but it was not so easy to prove it experimentally. In January 1937 Segre and his co-worker, mineralogist Carlo Perrier set about tackling the problem in earnest.

First they found that the samples of molybdenum from America were emitting beta-particles — fast electrons. That meant that the metal really contained a radioactive isotope, but what was it exactly? It could be an isotope of molybdenum proper or of other elements, such as zirconium, niobium and ruthenium, or of the missing element No.43.

A painstaking chemical "investigation" revealed that none of the "suspected" elements, except the last, had anything to do with the beta-radiation. After removing them, the scientists finally obtained the long-awaited "eka-manganese". But to say "obtained" is probably an exageration: as transpired later, they were dealing with 0.000 000 000 1 gram of the new element. On the other hand, for physicists one-ten-thousand millionths of a gram is not so little. It will be recalled, that the discovery of mendelevium (No.101) was registered when only 17 atoms of the element were obtained. An example to illustrate the point: if all the atoms of iron contained in a pin's head should be evenly distributed over the surface of the globe a good ten million (!) atoms will "settle down" on every square metre of the surface.

But back to the main subject. In June 1937 Segre and Perrier succeeded in artificially recreating the first of the "extinct" elements. Without much ado they gave element No.43 the name technetium (from the Greek technetos, artificial).

Although the amount of technetium the scientists possessed was really minute, they were able to learn something about its properties and realize that it was a relative of rhenium, moreover, quite a close relative.

The great desire of physicists and chemists throughout the world to learn more about the artificially created resident of the elements table was quite natural. But to study technetium it had to be had first. Irradiated molybdenum was clearly of no help — it was too poor in technetium. Something better had to be found.

The search did not take long: in 1940 Segre and his assistant Wu Tsien-hsun discovered that one of the longest-living isotopes of technetium was present in considerable amounts in the "splinters" formed during the bombardment of uranium with neutrons (the work of nuclear reactors). Every kilogram of the "splinters" contained a few grams of technetium. That was something meriting serious consideration. Small wonder, therefore, that nuclear reactors, apart from doing their main job, became something like technetium producing factories.

Their first product — a heavy, high-melting silvery-white metal cost a bit too much — thousands of times more than gold. But atomic power industry was developing fast, burning up more and more nuclear fuel every year and the "splinters" of uranium were becoming less and less scarce. The price of technetium began to drop sharply. But since the process of its extraction is exceptionally involved, it remained sufficiently high: in 1965 one gram of the "synthetic" metal on the world market was sold at 90 dollars. On the other hand, the amounts produced were now measured not in fractions of a milligram but in tens and hundreds of kilograms and scientists could now study its properties thoroughly and try to outline the likely spheres of its future activity.

Technetium's most important role — combatting corrosion — was discovered rather soon. Corrosion is a vicious predator, mercilessly devouring millions of tons of steel a year. True, metallurgy smelts stainless steel, a "dish" corrosion cannot digest. But this metal is much more expensive than ordinary steel and besides, there is use for different steels and to manufacture a metal which is corrosion- and wear-resistant is not always possible. Furthermore, the amount of chromium and nickel that would have to go into the making of stainless steel would be unreasonably large. Metal researchers, physicists and chemists are continuously searching for ways to curb corrosion, make it less greedy.

The problem of corrosion is a difficult one, but some important developments have been registered in this field. For example, it has been found that some substances make the metal's surface chemically

passive, thus reliably protecting it from corrosion. They have been termed inhibitors. Technetium has been proved to possess the highest inhibiting ability. If a steel part is treated with a solution containing traces of pertechnates (salts of technetium acid) as small as hundreds of thousandths of one per cent, the steel will be transformed into an impregnable fortress which will not be affected by corrosion even if it is heated to 250°C.

Another interesting property of technetium is its superconductivity. It is known that at temperatures close to absolute zero (—273.16°C) many metals become superconductors, that is, offer practically no resistance to the electric current. The higher the point of transition to the superconducting state the more promising the metal for industrial use. In this respect technetium has no competitors: it conducts electricity absolutely freely at 8.24 K (—264.92°C). Other metals have to "cool down" a little to acquire such an ability.

Scientists still entertain hopes of finding technetium in the earth's crust, since it is possible to suppose theoretically that "splinters" of uranium may also be formed naturally. Besides, it is quite possible that technetium may turn up in mountain rocks containing molybdenum, ruthenium and niobium: under the action of the neutrons coming to earth from outer space the isotopes of these elements may transform into the isotopes of element No.43.

It is hardly realistic, however, to set great store by our planet. This is why researchers have turned their attention to other space objects in search of technetium. In 1951 an American astronomer, Charlotte Moore, published a sensational paper on the discovery, by spectral analysis, of technetium on the Sun. A year later R. Merill of Britain

discovered the lines of this element in the spectra of some stars in the constellations Andromeda and Cetus. Although further studies failed to confirm Moore's discovery, hundreds of other spectrograms proved indisputably the presence of technetium on distant stars.

The most curious fact was that the stellar reserves of this element appeared to be perfectly comparable with those of zirconium, niobium and molybdenum. Could it be supposed that technetium from the Andromeda differed from the terrestrial in that it was stable, hence, could not disintegrate? No, that had to be ruled out. But perhaps these stars are much younger than the Earth and technetium has simply had no chance to transform into other elements? This must be ruled out too, since the stars we are talking about and our planet belong to the same "generation".

The only plausible explanation is that technetium is being formed in the depths of some celestial bodies at present as well. Science is yet powerless to explain how this process works and can only hypothesize. One theory is that thermonuclear reactions are constantly taking place in the depths of the stars in the process of their evolution and thus new chemical elements are born.

It is quite possible to suppose that somewhere in the expanses of the Universe, somewhere in far galaxies, there exists an unknown planet, with its surface ruffled by hillocks of solidified lava. The lava must contain "fresh" technetium erupted by volcanoes. Could we also suppose that dinosauri are grazing somewhere nearby?

Pd

AN ENGLISH SCIENTIST'S JOKE (PALLADIUM)

A fateful morning.— A strange ad.— Curiosity is no crime.— The swindler will be exposed!— How does one win prize money?— Demystification.— Chenevix's fiasco.— The name of the goddess was Pallas Athena.— The Spanish government's assignment.— Not much to show for it.— A modest part.— Are there spots on the Sun?— Everything is relative.— White gold.— Good connections.— Strong armour.— In an outer orbit.— Palladium works miracles.— All are pleased.— Something to think about.— Purple alloy.— Two medals.

That day Richard Chenevix, a successful English chemist, woke up earlier than usual. Heavy, dripping clouds hung low outside the windows. As if it was not content with rattling on the roof all night, the downpour continued into the day in a vain attempt to test the quality of London buildings. It seemed the heavens were determined to splash out all the water they could and more.

We should not have concentrated so much on the atmospheric phenomenon so typical of the misty Albion, had it not been for the fact that that wet morning in 1803 witnessed an event which was to damage Chenevix's scientific reputation.

Looking through the papers over his morning cup of coffee Chenevix came across an incredible advertisement, saying that Mr. Forster, a collector of minerals and trader, was selling in his shop, at a reasonable price, a new metal, palladium, which not a single chemist in the world had heard anything about only the day before.

Was it a joke, a scientific mystification or an advertising trick? Chenevix was absolutely sure there could be no new metal, but his curiosity took the better of him and he set out to the shop, the bad weather notwithstanding.

To his great surprise Forster really showed him a tiny ingot of a metal which resembled platinum but was much lighter, and explained that a few days previously he had received a letter written in beautiful handwriting on expensive stationery, in which an anonymous correspondent offered him to sell the enclosed small ingot of a hitherto unknown metal. That was all Forster could tell him. Chenevix decided to buy and analyze it and publicly ridicule the presumptuous alchemist who was claiming that he had discovered a new metal. Besides, he would teach a lesson to the shop owner for his part in the shameful fraud.

Chenevix informed his colleagues of his intention and they prepared to await results. Soon Chenevix published his paper reporting that the so-called palladium was not a new element, but an alloy of platinum with mercury. It would seem the fraud was exposed, but alas, no matter how hard other chemists tried to detect platinum and mercury in the mysterious metal, they failed. Stung by that development, Chenevix hurried to explain that he believed the mercury in the alloy had become so firmly fused with platinum that it was practically impossible to separate them. Moreover, he gave the recipe for the preparation of the alloy.

The furor round the new metal had gradually begun to subside when suddenly there was an announcement in a scientific journal setting a prize of 20 pounds (!) to one who would be able to prepare palladium from platinum and mercury within a year according to Chenevix's directions or by some other process. The number of people who wanted the money was large enough, but the year had passed and neither Chenevix nor anyone else had been able to produce the metal.

Shortly after the time limit had passed, in 1804, Secretary of the London Royal Society (i. e. Academy of Sciences), the well-known doctor and chemist William Wollaston, reported to a Society meeting that when analyzing platinum he had discovered a metal characterized by the same properties as the metal bought by Chenevix the previous year, and also another metal which he named rhodium. At the beginning of 1805 Wollaston sent an open letter to the journal that had published the announcement about the prize, in which he admitted that he was responsible for the excitement around palladium, the metal he had discovered, that he had given Forster the ingot to be sold and that it was also he who had set up the 20-pound prize.

It is hard to say what prompted Wollaston to announce his discovery in such an extraordinary way, but for Chenevix it proved disastrous: shaken by his blunder, he soon gave up chemistry altogether.

By giving the name palladium to the new metal, Wollaston paid tribute to the German astronomer, H. Olbers, who discovered a new asteroid in the solar system in 1802 and named it Pallas in honour of the Greek goddess of wisdom Pallas Athena.

Twenty years or so later the following item appeared in the *Gorny Journal* (Mining Journal) in Russia: "In 1822 G. Brean was instructed by the Spanish government to purify and melt into ingots all the platinum found over the years in America. Accordingly, when processing more than 61 poods* of raw platinum, Brean isolated two and a quarter pounds of palladium, the metal discovered by Wollaston and priced five and a half times higher than gold, owing to its extreme scarcity."

Today when it is possible to estimate the content of all the elements in the earth's crust more or less accurately, it is believed that the content of palladium is nearly ten times greater than that of gold. But the total reserves of palladium, like of the other metals of the platinum group, are rather meagre — only $5 \cdot 10^{-6}$ per cent, even though geochemists know nearly 30 minerals containing this element. Unlike other platinoids, palladium along with platinum occurs naturally. As a rule the native

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* 1 pood is 16.38 kg — *Ed.*

metal is admixed with platinum, iridium, gold and silver. Frequently palladium itself occurs as an admixture in natural platinum or gold. An extremely rare variety of native gold (porpezite), containing 8-11 per cent of palladium, has been found in Brazil.

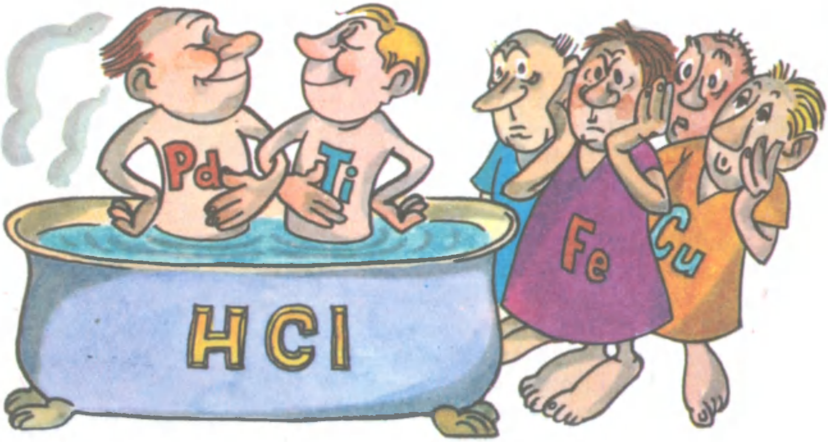
Since palladium placers are rather rare the main raw material for its extraction are the sulphide ores of nickel and copper. Of course, here palladium plays the modest part of a by-product, but this does not make it any less valuable. Transvaal and Canada have considerable deposits of such ores. Comparatively recently Soviet geologists discovered vast deposits of copper-nickel ores in the region of Norilsk which contain platinum metals, and mainly, palladium.

This element also occurs on other celestial bodies which is proved by the composition of meteoritic matter: iron meteorites contain up to 7.7 grams of palladium and rock meteorites, up to 3.5 grams per ton of matter. Everyone knows that there are spots on the Sun, but it is hardly common knowledge that there is also palladium. And yet, it is a fact that it was discovered there along with gelium as far back as 1868.

Being about one and a half times heavier than iron, palladium is nevertheless known as a light-weight among its "colleagues", the platinoids: in density (12 g/cm^3) it is considerably inferior to osmium (22.5 g/cm^3), iridium (22.4) and platinum (21.45). It also has a lower melting point than the other metals in the group (1 552°C). It is malleable even at room temperature. Since it is quite beautiful, takes a fine polish, does not tarnish or corrode, palladium is a favourite with jewellers who use it, among other things, in settings.

We are all used to such newspaper cliches as "black gold" for oil, "soft gold" for fur and "green gold" for forests. When they speak of "white gold" they usually mean cotton. But gold in fact can literally be white: even a small amount of palladium added to it removes the yellow tinge and gives it a beautiful white colour. White-gold watches, bracelets and settings for gems are extremely effective.

The association of palladium with titanium has proved very good. Titanium is known for its high corrosion resistance: even such "omnivores" as aqua regia or nitric acid cannot "have a bite" of titanium. However, it does corrode under the action of concentrated hydrochloric and sulphuric acids. But if it is "vitaminized" with palladium (an addition of less than 1 per cent) titanium's ability to resist these aggressors



increases drastically. This alloy is produced at Soviet plants for use in equipment operating in the chemical, oil and atomic industries. After a year in hydrochloric acid a plate made from the new metal loses only 0. 1 millimetre in thickness. Meanwhile pure titanium loses more than two millimetres to this aggressor a year.

Why is the influence of palladium on titanium so good? The explanation is the recently discovered phenomenon of self-passivation (self-defense) of metals: an addition of microdoses of noble metals, such as palladium, ruthenium and platinum, to alloys based on titanium, iron, chromium or lead, makes their corrosion resistance hundreds, thousands or even tens of thousands of times greater.

Workers at the laboratory of alloy corrosion of the Physical Chemistry Institute of the USSR Academy of Sciences tested the action of palladium on chronium steel, which if used in machine parts, is destroyed by many acids within a few days. What happens is that when the metal is immersed in an acid solution, its positive ions diffuse into the solution while the ions of liberated hydrogen diffuse from the solution into the metal's crystalline lattice and there readily combine with free electrons. Hydrogen gas formed in the process destroys the metal. When parts made from the same steel with a minute (fractions of a per cent) addition of palladium were placed in the solution, the corrosion of the metal lasted only a few seconds after which the reaction stopped. The study showed that the acid interacted with palladium, first and foremost, causing a very thin layer of oxide to form on the metal surface. It was as though the machine part "put on" a protective clothing. The steel armoured in this way became practically impregnable: the speed of corrosion process in boiling sulphuric acid was not more than a few tenths of one millimetre a year (regular steel would have lost several centimetres).

Palladium itself is easily influenced by some other elements as well. For instance, an addition of some related metals, such as ruthenium

(4 per cent) and rhodium (one per cent) almost doubles its tensile strength.

Alloys of palladium with other metals (mainly silver) are used in dentistry (they make excellent false teeth). The most important contact points in electronic devices, telephones and other equipment are coated with palladium. Made from this metal are various dies and spinnerets — caps with numerous openings through which specially prepared mass is pressed in the production of extra-thin wire or artificial fibre. Palladium is the material used in thermocouples and in some medical instruments.

The most interesting thing about palladium, however, are its unique chemical properties. Unlike all the other elements known to science today, it has 18 electrons in its outer orbit. In other words, its electron shell is filled to capacity, which explains its exceptional chemical stability. Under ordinary conditions even the omnipotent fluorine can do no more harm to it than a mosquito bite to an elephant. It is only aided by high temperatures (500°C and higher) that fluorine and other powerful oxidizers can react with palladium.

Palladium can absorb (occlude, as physicists and chemists say) staggering amounts of some gases, and especially, hydrogen. At room temperature a cubic centimetre of palladium is capable of absorbing something like 800 volumes of hydrogen. Such experiments, naturally, leave their trace on the metal: it swells, puffs out and cracks.

No less striking is another property of palladium associated with hydrogen. For instance, if hydrogen is pumped into a vessel made from palladium, then sealed and heated, it will seep through its walls, as easily as water through a sieve. At 240°C, 40 cubic centimetres of hydrogen per minute goes through a square centimetre of a palladium plate, one millimetre thick. With a rise in temperature the metal's permeability grows even more.

Like other platinum metals, palladium is an excellent catalyst. This property, combined with its ability to pass hydrogen, explains the phenomenon discovered recently by a group of Moscow chemists. It consists

in mutual acceleration of two reactions in the presence of one catalyst, in this case, palladium. It is almost as if the reactions help each other, while the substances taking part in them are not mixed.

Now suppose we have a container divided into two compartments by a palladium membrane. One of the compartments is filled with butene and the other with benzene. An avid absorber of hydrogen, palladium "wrenches" it from the molecules of butene, it passes through the membrane into the other compartment and there readily combines with the molecules of benzene. Butene, deprived of its hydrogen, transforms into butadiene (the raw material for the production of synthetic rubber), while benzene, having absorbed hydrogen, becomes cyclohexane (from which kapron and nylon are made). Combining with benzene, hydrogen produces heat. This means that to prevent the reaction from stopping, the heat has to be continuously removed. But butene gives up its hydrogen only in exchange for heat. Since both reactions take place "under the same roof", all heat produced in the first compartment is made use of in the second. An effective combination of these chemical and physical processes becomes possible thanks to the palladium membrane catalyst.

With the help of a palladium membrane catalyst it is possible to obtain super-pure hydrogen from crude oil and casing-head gas, which is essential, among other things, for the manufacture of semi-conductors and the production of super-pure metals.

Today palladium is not very expensive — its price is a fifth of the price of platinum. This is an important fact, making the metal more promising every year. The new spheres of its application are to be found by computers which easily cope with problems of this kind, provided they are supplied with the necessary material "to think about".

It is hardly surprising to anyone today that computers play chess, control production processes, translate from foreign languages and calculate the trajectories of space flights. Then why should they not create new alloys with unique properties?

This is precisely the task which was undertaken by workers at the Baikov Institute of Metallurgy of the USSR Academy of Sciences several years ago. First the necessary algorithms (a common tongue with the machine which takes orders) were worked out. Then research data concerning approximately 1 500 alloys, supplemented by information on the component metals (e. g. their atomic structure, melting points, types of crystalline lattices, etc.), were fed into the memory unit of the *Minsk-22* computer. Its job was to predict on the basis of these data what new combinations of metals could be made and to outline their main characteristics, which would amount to indicating the areas of their application.

Just imagine tackling such problems the way it was done in the past, that is, "by hand", by means of standard experiments. This would mean that every metal chosen for a certain reason would have to have some quantity of another metal added to it, that samples would have to be prepared from the alloys obtained as a result and that, finally, those samples would have to be studied chemically and physically. And what if possible combinations not of two but of three, four or five components would have to be studied? That would truly be a Herculean labour and it would take scores of years or perhaps, even centuries. This is not to mention the great amounts of metals, some scarce and expensive, that the job would require. It is quite possible that nature simply does not have enough of such elements as rhenium, indium or palladium.

Meanwhile, a computer's "food for thought" are figures, symbols and formulas, while its "labour productivity", is, naturally, incomparably higher — it is capable of turning out vast scientific information within moments.

Owing to the extremely involved work carried out under Ye. M. Savitsky, corresponding member of the USSR Academy of Sciences, it was possible by means of computers to predict and then create in reality some unique alloys.

Among the first "computer-born" metals were palladium alloys, including the exceptionally beautiful lilac-coloured alloy of palladium with indium. But colour is certainly not the most important thing about the new metal "workers". Much more important are their business qualities. And it must be said that they are up to mark. For instance, one of the new metals developed at the Baikov Institute of Metallurgy — an alloy of palladium with tungsten — increases the reliability and life of many electronic instruments 20 times.

"Computer prediction", writes Savitsky, "naturally, is not used for alloys that can be obtained by a simple mixing of components. But where complex combinations are needed, concerned with the production of alloys that can endure great pressures and super-high temperatures and resist magnetic and electric fields, the help of computers is indispensable." Nearly 800 new superconducting compounds and almost 1 000 alloys with special magnetic properties have already been predicted by computers. Apart from that, computers have "suggested" the study of 5 000 combinations of rare-earth metals, of which only a fifth part is known to date. Valuable directions have also been given with regard to the transuranic elements.

According to Savitsky, "the possibilities of synthesis of nonorganic compounds are boundless. The number of compounds obtained this way may be increased tens of times already in the next few years. It is beyond doubt that they will include substances with absolutely new and rare physical and chemical properties, essential for the national economy and modern technology."

To wind up our story about palladium we will tell you about the history of two medals made from palladium. The first, in honour of Wollaston, was instituted by the London Geological Society one and a half centuries ago. First it was minted from gold, but after an English metallurgist, Johnson, extracted pure palladium from Brazilian porpezite, it was made only from this metal. In 1943 the Wollaston medal was awarded to the outstanding Soviet geochemist and mineralogist, Academician Fersmann, and is now kept in the USSR State Historical Museum. The second palladium medal — for outstanding work in electrochemistry and the theory of corrosion processes — was instituted by the American Electrochemical Society. In 1959 this medal was awarded to the leading Soviet electrochemist, Academician A. N. Frumkin.

Cd

NAMED AFTER CADMUS OF PHOENICIA (CADMIUM)

A stern inspector.— The mystery of the yellow residue.— As related by myths.— Claims to priority.— *Cri de coeur.*— A reliable alibi.— A cadmium coat.— An unwelcome guest.— Whiskers become fashionable.— A strong cobweb.— Nickel-cadmium cells.— A new razor for spacemen.— A reliable pacemaker.— Looking for fingerprints.— The trio at work.— Inside the nuclear reactor.— A job in an outlying area.— Beacon lights.— Exorbitant prices.—"Made in space".— The negative aspect.— A great rarity.

It all began with an inspection. But we must warn lovers of whodunits that they are in for a disappointment: that particular inspection did not result in the capture of a gang of crooks but... in the discovery of a new chemical element.

It happened in Germany at the break of the last century. A district physician, Rolow, who was inspecting the district chemist's shops in his official capacity, found that many of them sold preparations containing zinc oxide which, he suspected, might contain arsenic. Since this element had always been notorious because of the numerous sinister stories associated with it (it is still believed by many historians, for instance, that arsenic was the cause of Napoleon's death), Rolow prohibited the selling of the preparations and analyzed the oxide he had confiscated. The very first experiments carried out by the vigilant doctor seemed to confirm that his precaution was well-founded: acting with hydrogen sulphide on the oxide, he obtained a yellow precipitate strongly resembling the sulphide of arsenic. But the owner of the factory manufacturing the ill-fated preparations, one Hermann, was not going to give in without a fight. A chemist by profession, he carefully checked his products for arsenic, employing all methods known then. The results clearly refuted Rolow's view and Hermann turned to the local authorities requesting them to "rehabilitate" his innocent preparations.

Before making a definite ruling, the authorities of the province of Hannover deemed it necessary to seek the opinion of Professor Stromeyer, who chaired the chemistry department at Göttingen University and, as a part-time job, held the post of Inspector General of all Hanover chemist's shops.

Samples of the preparations containing zinc oxide were sent from Schönebek where Hermann's factory was situated, to Göttingen and the Inspector General set to his task of arbitration. To obtain zinc oxide

chemists in Schönebek calcinated zinc carbonate. Stromeyer went the same way and, to his surprise, discovered that the resultant compound was yellow, while zinc oxide had to be white.

Hermann explained the colour by the presence of iron in the compound. Rolow insisted that it was arsenic. Stromeyer carried out the complete analysis of the zinc carbonate and discovered a new metal, which looked very much like zinc, but could easily be separated from it by means of hydrogen sulphide. The scientist named it cadmium, by this stressing its relation to zinc: from ancient times *cadmea* in Greek meant zinc ore. As legend has it, the word originated from a Phoenician, Cadmus, who was said to be the first to have found a zinc rock and to notice that it gave a golden tinge to copper during smelting. Another Cadmus was a mythical hero who had overcome the Dragon in a hard battle and on his land built the fortress of Cadmea round which the seven-gated city of Thebes grew up afterwords.

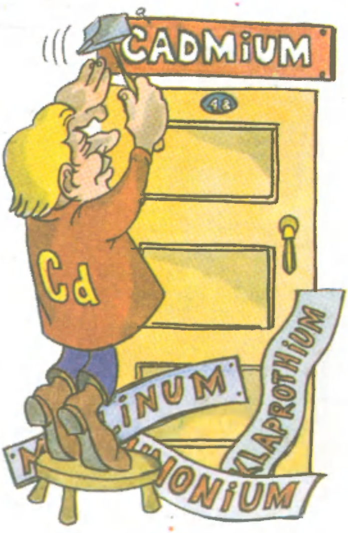
In 1818 Stromeyer published his paper with a detailed description of the new metal, and soon after, several claimants to priority in the discovery turned up. The first was Rolow we have mentioned, but his claims were rejected as unfounded. A little later than Stromeyer and independently of him the German chemist Kersten found the new metal in the zinc ores of Silesia and suggested that it should be named *melinum* (yellow like quince) by the colour of its sulphide. Two other scientists, Gilbert and John, also discovered traces of the new element. One of them proposed that it should be named junonium (after the asteroid Juno discovered in 1804) and the other klaprothium (in honour of the well-known German chemist Martin Klaproth, the discoverer of uranium, zirconium and titanium). But Klaproth's great services to science notwithstanding, his name was not fated to be given to a chemical element and cadmium remained cadmium.

The pure metal is rather heavy (heavier than iron) and soft. If bent, a rod of cadmium emits a crackling sound caused by deformation of its crystals. The same property is observed in tin (the “cry of tin”).

Its relatively low melting point (321°C) allows for an extensive application of cadmium as a component in low-melting alloys. Among them, Wood’s alloy (12.5 per cent of cadmium) was developed as far back as 1860 by not a very well-known British engineer, Wood. This is perhaps the reason why his metal is often ascribed to the famous American physicist, Wood. But the latter has a very reliable “alibi”: he was born 8 years after the alloy was manufactured. Low-melting alloys are used as solders and as the material for delicate and intricate castings, as well as in automatic fire-warning systems and in glass-to-metal seals.

Cadmium alloys have good anti-friction characteristics. An alloy of 99 per cent of cadmium and one per cent of nickel is used in bearings for the automobile, aircraft and marine engines. Bearings made of cadmium-based alloys are sometimes coated with indium to protect them from the harmful action of organic acids contained in lubricants. On the other hand, cadmium coating is a reliable protection from atmospheric corrosion for iron and steel goods. In the past a cadmium coating was deposited by immersing a metal in molten cadmium, but today this process is carried out only electrolytically. A coating of cadmium covers the most vital parts on aircraft and ships, and also various goods intended for use in tropical climates. Curiously, cadmium coatings are especially effective in natural surroundings: in rural areas their corrosion-resistance is much higher than in industrial areas. Cadmium-plated tin is very welcome in a number of industries, but owing to the metal’s toxicity it is completely barred from the food industry. In some countries this rule has even been formalized in law.

Until recently cadmium platings had one flaw that made itself felt every now and then. What happened was that during the process of electrolytic deposition of cadmium on a steel part the hydrogen of the electrolyte could diffuse into the metal. That extremely unwelcome guest caused super-strong steels to contract a dangerous “disease”— hydrogen embrittlement resulting in a sudden destruction of the metal under load. Thus, on the one hand, cadmium plating reliably protected the part from corrosion and, on the other, created the danger of its premature break-down. That was why engineers were often compelled to do without cadmium’s services.

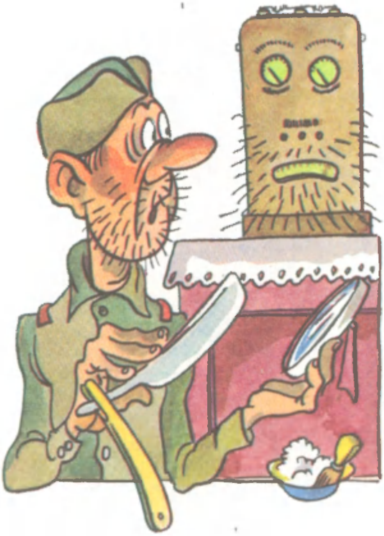


Workers at the Institute of Physical Chemistry of the USSR Academy of Sciences have succeeded in finding a “cure” for this disease. It appears that if one atom of titanium is added to a layer of cadmium containing 1 000 atoms of cadmium, the steel part is immune to hydrogen embrittlement, since during the process of electroplating titanium manages to absorb all the hydrogen from the steel.

An important landmark in the history of filamentary crystals is associated with cadmium. It was noticed as early as the Second World War that sometimes electronic equipment went out of service for no apparent reason. It was found that the trouble was caused by minute (1-2 microns in diameter) crystals of tin or cadmium that sometimes grew on the surface of steel parts coated with one of these metals.

To successfully combat the filamentary crystals, or "cat whiskers" as the harmful metal "growth" came to be known, it was essential first to study them. And so the "whiskers" became the object of numerous studies and soon it was found (really, every cloud has a silver lining) that they were characterized by exceptional, close to theoretical, strength. This fact brought about a dramatic change in the attitude to the "whiskers", and soon effective methods of growing them were developed and found extremely useful in many fields of technology. Since then filamentary crystals of hundreds of elements and compounds have been grown in the laboratories of many countries, but the most important of them are tin and cadmium ones that were the first to attract the interest of science.

Millions of kilometres of copper wiring entangle our cities: owing to this "cobweb" trolleybuses and trams are running through the streets in all directions. Meanwhile their current collectors are mercilessly galling the copper wiring, causing it to wear out fast. This is where cadmium comes in handy: small additions of this element (about one per cent) considerably increase the strength and hardness of the copper, while having practically no adverse effect on its electric properties. Wiring from copper with cadmium serves for many years without replacement even on the busiest transport thoroughfares.



Modern technology is inconceivable without storage cells. They are essential in spaceships and submarines, motor vehicles and radio sets, telephone and telegraph installations, miner's lamps and hearing aids, photographic flares and signal lights — to list all the applications of storage cells is as "simple" as to count all the stars in the sky. These simple devices consisting of two electrodes immersed in an electrolytic solution accumulate electric energy, transform it into chemical energy and

then back into electricity as required. Nickel-cadmium cells are among the most extensively used. In them the negatively-charged plate, i. e. electrode, is an iron grid filled with sponge-cadmium and the positively-charged plates are coated with nickel oxide. The electrolyte is caustic potash. Such cells are distinguished by excellent performance, great reliability and long life, and they take only 15 minutes to charge.

Doctors have found an even more interesting use for the nickel-cadmium cell. Fitted into a pacemaker and introduced into the chest of a heart patient, this miniature power station supplies it with energy. But a cell cannot work indefinitely — it has to be recharged from time to time. Does this mean that the patient has to lie down on the operating table every time this has to be done? Certainly not. To keep the cell going the person concerned has to wear a special magnetic jacket for an hour and a half every week. Thousands of people have already seen from their own experience the advantages of the new pacemakers.

Recently cadmium began to be used by British criminalists: surfaces dusted with extremely fine cadmium powder reveal very clear fingerprints.

Cadmium compounds are the principal components in the Weston cell which is something like a standard of electromotive force (emf). It consists of an amalgam of cadmium, cadmium sulphate crystals and an aqueous solution of this salt. At room temperature the emf characteristics fluctuate within a very narrow range.

The middle of this century was marked by unprecedented scientific and technological progress, the highest summit of which was the harnessing of the energy of the atom. To subdue the fantastic forces contained in the atomic nucleus required not only the minds of geniuses but also materials with unique properties. Cadmium was one of the few metals that was applied by the designers of nuclear reactors.

What is the role of this metal in the atomic industry? A reactor cannot operate without control rods regulating the neutron flux any more than an automobile can operate without its brakes. To trigger off the reaction the rods are slowly raised, thereby enabling the neutrons to "rush about" in the reactor. But if they "get out of hand", that is, if the rate of the reaction becomes too fast, the rods are again lowered into the active core with the result that the neutrons become locked up, as it were, and the reaction is slowed down.

Every reactor also has a massive safety rod which is activated in the event the control rods fail to operate. But what if the safety rod also fails? This is exactly what happened at the American atomic centre in California. Due to a fault in the design, the safety rod failed to sink into the active core and the chain reaction got out of control, creating a grave danger to the local population. People had to be urgently evacuated from the dangerous zone until the nuclear "fire" was put out. Fortunately, there were no victims, but a tremendous loss was incurred and the reactor itself was put out of order for a time. Had the safety rod been in working order, the neutrons would have been pacified within moments.

The main demand made on the material from which the control and safety rods are made is the ability to absorb neutrons and cadmium is one of the "biggest specialists" in this field. There is only one reservation: this concerns only thermal neutrons whose energy is very small (it is measured in hundredths of a fraction of an electron-volt). In the first years of the atomic era nuclear reactors worked on thermal neutrons and for a long time cadmium played the "first fiddle" among the materials used for nuclear reactor rods. Later it had to give up its leading role to boron and its compounds. But atomic physicists, nevertheless, have been discovering more and more spheres of activity for cadmium. For example, a cadmium plate placed in the way of a neutron flux makes it possible to study its energy distribution and its uniformity, and to determine the proportion of thermal neutrons.

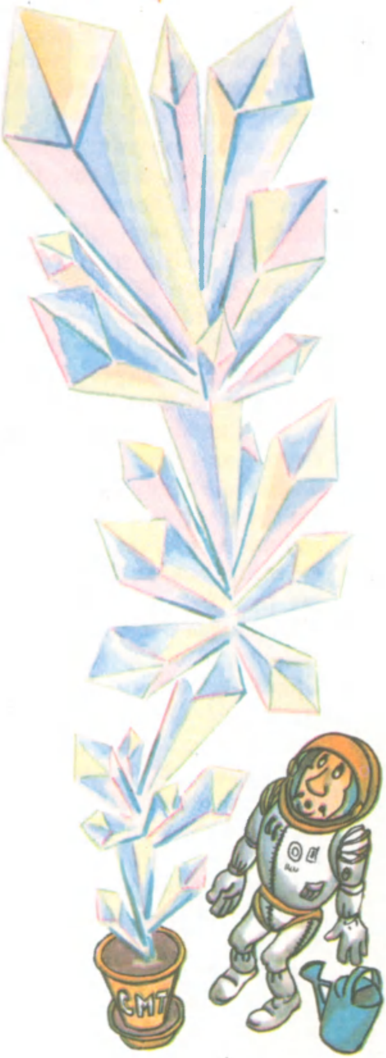
While the nuclear power industry is something like an epicentre of modern technology, the paint and varnish industry is only a perifery. And yet here too cadmium works as conscientiously as in its responsible jobs in the nuclear reactors. Cadmium sulphide was used as a mineral pigment even back in the last century. The *Technical Encyclopaedia* printed in the early 1900s contains the following item: "... pale-yellow tinges, beginning from lemon-yellow and on, are obtained from weakly acid and neutral solutions of the sulphate of cadmium and, when precipitated by sodium sulphide, produce darker yellows... Cadmium yellow of six hues — from lemon-yellow to orange, can be produced by one or another method. In its ready form this pigment has a beautiful shiny yellow colour. It is rather stable in weak alkalis and acids and is absolutely insensitive to hydrogen sulphide; therefore, dry-mixed with ultramarine, it gives a splendid green pigment, called commercially cadmium green... Mixed with drying oil, it becomes a house paint; it has a fine covering power, but being very expensive (5 to 6.50 roubles a pound), it is mostly used in art in the form of oil paint of watercolour, and also in printing. Owing to its great refractoriness, it is likewise applied in painting on chinaware..."

In later times cadmium sulphide continued to be valued as a paint, especially by railway carriage builders, who had used it on their goods for years. That was to be explained no so much by that "it has a fine covering power", but by its high resistance to the "bad influence" of the locomotive smoke. Of late the relatively expensive pure cadmium sulphide has been replaced by cheaper pigments — cadmopone and zinc-cadmium lithopone, the latter of a pretty ivory colour.

Cadmium sulphide is widely used in pyrotechnics, owing to its ability to give a dark blue or, if certain substances are added, a pale blue or purple light. But the potentials of cadmium compounds are not restricted to this job. Combined with selenium, it makes a red pigment. It is to this compound that the stars on the Moscow Kremlin owe their ruby colour. In other words, cadmium has "friendly contacts" with all the colours of the rainbow and cadmium pigments are used for the dyeing of rubber, plastics and synthetic fibres.

The same salts of cadmium — sulphide and selenide — are also known for their semiconducting properties. Scientists suggest that crystals of cadmium sulphide are destined to make an important contribution to the development of electronics, nuclear physics and acoustics (particularly, as amplifiers of ultrasound).

It is likely that the cadmium sulphide is to have its say in the solution of the problem of conversion of solar into electric energy — the object of intensive research in many countries, for it is a fact that only 0.001 per cent of the colossal energy emitted by the Sun is put to use. Really, nothing to boast about. It was for good reason that the outstanding French physicist Frederic Joliot-Curie, who had devoted all his life to getting energy from the atomic nucleus, said that "the solution of the problem



of utilization of solar energy is more important to humanity than harnessing the energy of the atomic nucleus." Solar cells have already been.designed for spaceships. The beacons on Kamchatka and the Kurile islands now work on solar energy, as well: two or three months of sunny weather enable the beacons to function for a whole year. Since the silicon cells mostly applied for this purpose are very expensive and make the free energy of the Sun rather dear, physicists have proposed a number of other and much cheaper ones. For example, in the United States solar cells have been designed in the form of a thin film based on the sulphides of cadmium and copper. Although they are not very efficient yet, specialists are confident they can be improved.

The recent tendency is to carry out many technical experiments not in terrestrial laboratories but in space. One of the characters in a science-fiction story *Beyond the Earth* by Konstantin Tsiolkovsky (1857-1935) says: "Here (in space) we have a marvellous possibility to carry out all kinds of metallurgical work." Only thirty or forty years have passed since then and the product of a great scientist's imagination has become reality. Weightlessness is indeed a unique medium for scientific and technical experiments. But since the capacity of space laboratories is not very impressive yet, the "participants" in extraterrestrial experimentation have to be very carefully selected from among the most interesting and promising materials. Cadmium has been lucky: the program of a space study of materials includes production of a number of semiconducting materials, including the telluride and sulphide of cadmium, as well as of a cadmium, mercury and tellurium (CMT) compound — all by means of the "*Splav*" (Alloy) and "*Kristall*" (Crystal) installations on board the *Salyut-6* orbital station.

Scientists are particularly interested in the growing of the CMT crystal which is a solid solution of the tellurides of cadmium and mercury. This is a semiconductor material which is indispensable in the manufacture of infrared imagers — instruments of great precision applied in medicine, geology, astronomy, electronics, radioengineering and many other fields. It is extremely difficult to obtain it in terrestrial conditions: owing to the great differences in their density, its components cannot fuse and instead of a uniform material scientists sometimes get a three-layer "pie". For the sake of one tiny crystal they have to grow a large one, to cut out the thinnest boundary layer from it and throw the rest away. And there is no other way: the purity and uniformity of the crystal is assessed in hundreds of millionths of one per cent. Small wonder that on the world market one gram of these crystals costs 8 000 dollars.

That was why scientists set such great store by weightlessness where the components of the crystal have absolutely no "reason" to compete with each other: they cease to be light or heavy. To create absolute "gravitational quiet" on board the *Salyut* during the hours the crystal was growing, the Flight Control Centre saw to it that the station did not jerk or turn about, reorientate itself or switch on its on-board engines. The spacemen themselves were not allowed to do any physical exercises on the running track and the ergometric bicycle.

The scientists' effort brought good results: as the preliminary analysis of the samples returned to earth has shown, the crystals obtained in space are large enough and have a regular structure. So far they have not been used for industrial needs but have been sent out to dozens of laboratories for a careful study. Nevertheless, it can be stated for sure that the time is not far off when space-born crystals will be in operation in many instruments.

There are negative aspects in the many-sided activity of cadmium too. Several years ago an employee of the American health service found that there was a direct connection between mortality from cardio-vascular diseases and... the content of cadmium in the atmosphere. His findings were based on a study of the residents of 28 American cities. In four of them — Chicago, New York, Philadelphia and Indianapolis — the cadmium content was much higher than in the rest of the cities studied and so was mortality from heart diseases.

Once the enemy is spotted, it has to be combatted. The first experiments carried out by the American scientists working on the project were intended to clear the water of a Mississippi bay from cadmium and mercury. This purpose was to be served by water hyacinths, the flowers picked by the experimenters because of their ability to grow extraordinarily fast. But since no results have been reported yet, it is for the future to show how effective the "flower method" is.

While doctors and biologists are trying to determine if cadmium is harmful to health and seeking ways of lowering its content in the environment, technologists are sparing no effort to increase its production. Just compare: in the second half of the last century only 160 tons of cadmium were produced annually; at the end of the 1920s its production in the capitalist countries was already around 700 tons; and in the 1950s it reached 7 000 tons (this is when cadmium came to be regarded as a strategic material for the rods of nuclear reactors).

In nature cadmium is scarce and rather widely dispersed. Its content in the earth's crust is immeasurably lower than that of, say, beryllium, scandium, germanium or cesium. Even the content of indium, which is considered to be one of the scarcest elements, is greater than that of cadmium. Cadmium-containing minerals are very few, and most often cadmium is present in zinc, lead-zinc and copper-zinc ores. The metal is obtained as a by-product during the processing of these ores, but, as you have doubtlessly noticed, this doesn't make it any less valuable.

In

ASSOCIATED WITH THE LAND OF WONDERS (INDIUM)

Napoleon is prepared to loosen his purse-strings.— But fortune held.— How much is a pencil?— A troublesome element.— Radioactivity no longer concealed.— Strictly a trace element.— A find in Arizona.— Puncturing the mist over the British Isles.— The fire brigade can go to sleep.— Physicists are baffled.— In an underwater kingdom.— Bearings must be protected.— A few words on dental fillings.— A metal blanket.— Green gold.— Measuring a neutron flux.— A pure impurity.— A wonderful crystal.— Born of dust.— Has a football anything to do with it?— Always a welcome guest.

Indigo, the deep blue dye brought from the fabulous land of India, had been highly valued in Europe from time immemorial. In purity of colour it could vie with the blue lines of the solar spectrum. Owners of textile mills did not stint money to buy the "queen of all dyes" which they used for their woollen cloth and other textiles. At the end of the 18th century when the sea routes from Europe to India and other southern countries were blocked by the British navy, indigo and other overseas goods became very scarce. Wishing to preserve the traditional dark blue army uniform, Napoleon promised one million franks (a colossal prize for those times) to one who would find a method of making the wonderful dye from a European raw material.

The reason we began our story about indium with an allusion to indigo is that it was the colour of this dye that gave element No. 49 its name.

In a small German town of Freiburg, in 1863, Professor Reich and his assistant Richter were busy in their laboratory one day with a spectroscopic observation of some zinc minerals found in the mountains of Saxony. They were looking for the element thallium discovered two years previously. Analyzing one sample after another, they still failed to detect the deep green lines of thallium in the spectra. And yet fortune was with them that day and finally their effort was rewarded. In one of the spectra they saw an exceedingly bright blue line, not belonging to a single element known then. The two chemists realized they had discovered a new element. Owing to the deep blue colour of the new element's spectral line, it was given the name indium.

The problem facing the scientists now was to isolate the metal. It was quite a while before they could produce two ingots of metallic indium, each the size and shape of a pencil. The similarity with the pencil was not only in appearance: indium turned out to be an uncommonly soft metal — almost five times softer than lead and 20 times softer than pure gold. Of the ten minerals on the Mohs hardness scale, nine are harder than indium and only one, talc, is softer. Though indium leaves a trace on paper, it would be as ridiculous to write with an indium pencil as to fuel a stove with money: the French Academy of Sciences priced the samples of the new metal at 80 000 dollars or 700 dollars a gram.

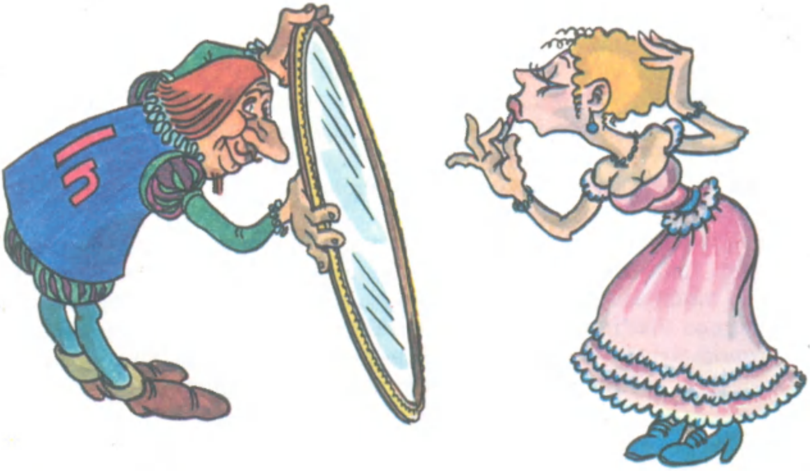
When indium made its first appearance in the world nobody suspected, naturally, that it could confuse Mendeleyev. But indium was not to blame so much as its discoverers who took it to be a close relative of zinc and assumed that it was also bivalent. Furthermore, their conclusion that the atomic weight of the new element was 75.6 was also erroneous. If that were so, then there was no place for indium in the periodic table.

Mendeleyev suggested that indium was trivalent, that in its properties it was much closer to aluminium and that its atomic weight was 114. That was one of the many cases when Mendeleyev made important corrections in the characteristics of known elements on the basis of the periodic law he had discovered. Subsequent experience confirmed Mendeleyev's belief: the atomic weight of indium, established on the basis of the most accurate methods, was 114.82. The element was placed in square No.49 in the third row of the elements table.

Natural indium consists of two isotopes with mass numbers 113 and 115, the proportion of the latter being much greater than of the former — 95.7 per cent. Up to the middle of the century both these isotopes were believed to be stable. But in 1951 indium-115 was found to be subject to beta-decay, which caused it gradually to transform into tin-115, though this process is extremely slow: the half-life of the nuclei of indium-115 is $6 \cdot 10^{14}$ years. At this rate of transformation it is only natural that indium "managed" to conceal its radioactivity for so long. Since then physicists have been able to obtain some 20 radioactive isotopes of indium: the half-life of the one with the longest period of radioactive decay (indium-114) is 49 days.

Like many other metals, indium found no practical application for a long time. There are good reasons to explain it: it is not only scarce (in content in the earth's crust it is somewhere near the 70th place among the elements in the periodic table), but also greatly scattered, having practically no naturally occurring minerals in which it would be the main or one of the main components. At best it is only a trace element associated with the ores of other metals, in amounts not higher than 0.05 per cent. The difficulty involved in isolating such minute quantities from the ores is only too easy to imagine.

But the properties of indium being what they are, it could not be ignored by workers in the world of technology. In 1924 an American engineer, Murry, who travelled all over the United States in search of indium-containing ores, discovered concentrations of this trace element in the sand dunes of Arizona. True, the concentrations were not very



high, but still they were higher than in other places and soon a factory for the production of indium was commissioned there.

One of the first uses of indium was in high-quality mirrors for telescopes, searchlights, reflectors and other such equipment. This is due to the fact that ordinary mirror glass reflects different colours differently. This means that clothes, for instance, do not look the same in a mirror as in reality.

True, a woman sitting in front of a trellis will not notice the difference, but for many instruments colour falsification is simply inadmissible. This shortcoming is typical of most mirrors, including silver, tin and mercury-bismuth ones. Indium, meanwhile, is not only an extremely good reflector but is also absolutely "objective" with regard to all the colours of the rainbow — from red to purple. Indium mirrors in telescopes prevent any distortions in astronomical observations.

Unlike silver, indium does not tarnish in the air and retains a high reflection factor. It will be recalled that indium played an important part in protecting London from massive German air raids during the last World war. In their chase of the air pirats, the searchlights of the air defence, equipped with indium mirrors, easily punctured the thick mist often blanketing the British Isles. Since the melting point of the metal is rather low (156°C), the searchlight mirrors were in constant need of cooling, but considering the number of German planes brought down, the British War Office willingly spent all the money that was needed.

It must be said that a low melting point is sometimes an advantage and not a drawback. An alloy of indium, bismuth, lead, tin and cadmium melts at 46.8°C, owing to which it is a good automatic cut-out, protecting important junctions and machine parts from overheating. An alloy of indium with gallium and tin remains liquid even at room temperature, its melting point being 10.6°C. Fuses made from indium alloys are widely employed in fire-alarm systems.

Interesting experiments involving indium's low melting point were carried out in Canada. While studying particles of this metal in an electronic microscope, the Canadian physicists discovered that when the size of a particle was less than a certain value its melting point dropped sharply. Particles not larger than 30 angstrom would melt at a little above 40°C. A drop of more than a hundred degrees (from 156 to 40°C) naturally fascinates scientists. Even modern physics with its astonishing amount of information cannot explain the nature of this phenomenon. Perhaps it is so because its theory of melting processes is true only for matter of considerable mass and the Canadian physicists studied "gomeopatic" doses of the metal — only a few thousand atoms.

One of the valuable properties of indium is its resistance to the action of caustic alkalis and sea water. Copper alloys with a small addition of indium acquire the same characteristic. A ship's sheathing made from such an alloy remains unaffected by sea water for a long time.

Bearings in aircraft engines operate in rigorous conditions: the shaft makes several thousand revolutions in one minute, heating up the metal and lowering its resistance to the action of the lubricants. To protect the bearings from wear scientists have proposed a thin coating of indium, since its atoms, apart from making a tight layer on the working surface of the bearing, also penetrate into the depth of the metal forming a strong alloy. This metal cannot be affected by the lubricant and the life of the bearings is extended five times.

Indium is important in dentistry. Indium alloys (with silver, tin, copper and zinc), characterized by great strength and corrosion resistance, make excellent fillings. The role of indium in these alloys is to reduce to the minimum shrinkage of the metal when the filling solidifies.

Aircraft designers have many uses for the sinc-indium alloy — a corrosion-resistant coating for steel propellers. A very thin layer of an alloy of tin with indium oxide reliably protects the windshields. Under this "blanket" the glass does not freeze and remains clear from

ice. Indium alloys are also applied in glass and glass-to-metal seals (e. g. in vacuum engineering).

Some indium alloys are very beautiful, hence their application in jewelry. An alloy of 75 per cent of gold, 20 per cent of silver and 5 per cent of indium is called green gold. The American firm Studebaker has replaced chromium with indium in the plating on the exposed parts of automobiles, thereby considerably extending their service life.

In atomic reactors indium foil is used to measure the intensity of the flux of thermal neutrons and its energy: colliding with the nuclei of stable isotopes of indium, the neutrons transform them into radioactive ones, giving rise to electron radiation, its energy and intensity corresponding to those of the neutron flux.

But the most important application of indium is in the semiconductor industry. Indium of high purity is indispensable in germanium rectifiers and amplifiers where indium is an "impurity" securing hole conduction in germanium. The metal used for this purpose itself contains practically no impurities, or its purity is expressed, as chemists put it, by "six nines" (99.9999 per cent!). Some indium compounds (sulphide, selenide, antimonide and phosphide) are themselves semiconductor materials used in thermocouples and in some other devices. The antimonide of indium is the basis of infrared detectors capable of "seeing" slightly warmed objects in darkness.

Indium is one of the few chemical elements which have been "sent on a mission" to outer space and destined to usher a new stage in the industry of non-organic materials. In an interview to a TASS correspondent not long before the Soviet-American joint flight under the *Soyuz-Appolo* program in 1975 the crew captains Alexei Leonov and Thomas Stafford spoke on the significance of the experiments that were to be carried out on board the ship in orbit, particularly in the melting of metals and growing of crystals of various substances. "We are going to find out", said Alexei Leonov, "about the possibilities of obtaining new materials, metal and semiconductor ones. The Soviet and American spacemen believe that in space it is possible to fuse components that cannot be fused here on earth, and to create refractory materials..." The American astronauts on board the *Skylab* station, noted Stafford, conducted experiments on growing crystals of antimonide of indium and succeeded in obtaining a crystal that was the purest and strongest of all ever grown in terrestrial conditions.

Later, between 1978 and 1980,

new experiments involving indium and its compounds were carried out by the crew of the *Salyut-6* station.

Experiments with indium compounds continued on earth as well. Not long ago it was discovered that under the pressure of 30 000 atmospheres antimonide of indium changed its crystalline lattice owing to which its electric conductivity jumped one million times (!).

So far the world production of indium has not been large — just a few dozens of tons a year. This most valuable metal is generally obtained as a ... by-product in the processing of zinc, lead, copper and tin ores. Scientists in the German Democratic Republic have suggested an interesting method of producing this metal: it is obtained from the dust accumulating over one of the plants processing cuprous shales. First hot sulphuric acid is flushed through the dust containing indium and then sent on a long cycle of complex transformations as a result of which the pure metal is extracted.

The interest in indium is growing all the time, as more and more is learned about this metal. A few years ago US physicists found that the shape of its nucleus resembles a football with a band along the "equator".

Even though indium is a metal rarely occurring in nature, we can state for sure that its role in industry will grow year by year.

Sb

ONCE IN SCHTALHAUSEN MONASTERY (ANTIMONY)

A vain dream.— The tricks of a cunning monk.— Version over version.— In the service of cosmetics.— In ancient Babylonia.— “The Triamphal Car of Antimony.”— A shortage of celestial bodies.— Deceptive appearance.— The wolf snaps its teeth.— No antimony spots on the Sun.— A discovery in Kirghizia.— Not difficult but bothersome.— Travelling impurities.— Standard of purity.— Predisposed to filling out.— Some shrapnel into the bargain.— Babbitts have not been forgotten.— Studying a bullet trace.— A fire-resistant curtain.— A fire-work display.— Bacteria at work.

The search for the “philosopher’s stone” seized medieval Europe like an epidemics. The idea to find a substance whose action on almost any metal could transmutate it into gold was no end alluring. Those in the service of God were the most dedicated searchers, though it would seem they should find it beneath themselves to follow the example of their lay brothers in the lust for wealth. In those days it was hardly possible to find even one monastery in which the cells and basements were not used as alchemic laboratories. Day in and day out colourful liquids were boiling in retorts, suspicious substances were being crushed and mixed in mortars, but the miraculous stone remained a dream as much as ever.

Giving up the thought of saving his soul for a time, Father Leonardus, the dean of Schtalhausen Monastery, wholly committed himself to the search for a correct recipe for the “philosopher’s stone”.The humble father had tried out dozens of methods, but success evaded him. One day he had an inspiration: “What if I mix the ashes of the heretic burned yesterday with the ashes of his cat (burned together with its master as a lesson to other such creatures) and add a double quantity of earth from beneath the fire...” That strictly scientific approach, he thought, would definitely reward him. He carefully mixed the ashes with the earth and after some other essential manipulations, warmed up the mixture and sat back patiently waiting for it to cool and transform into an etherial, transparent substance: that was how the “philosopher’s stone” should look according to some leading specialists. But unfortunately the devil must have been lurking somewhere nearby: on cooling, the mixture became a heavy dark substance with a metallic lustre. Peeved with yet another failure, the mortified dean threw out the fruit of his labours in the back of the monastery yard.

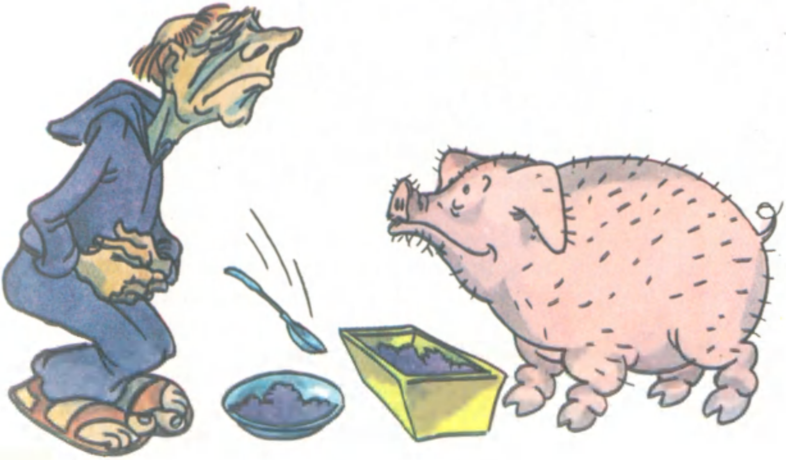
Days passed. Strolling up and down the yard during a break between his scientific experiments and prayers one day, Father Leonardus noticed that some monastery pigs were licking the substance he had thrown away with obvious relish. And he immediately recalled that in general the pigs were looking much more content lately.

"Surely this stone must be edible," guessed the cunning cleric. "If I can feed a little of it to my monks, I'll be better off even without the "philosopher's stone!" Why put off a good work? And he ran back to his cell and quickly prepared another helping of his dish. The very next morning 40 hungry monks had porridge with the wonderful seasoning. But darn that devil! Of course, he was not asleep: the next morning all forty died a horrible death. Only then did Leonardus realize what sin he had committed and vowed never to conduct any chemical experiments. As for his ill-fated "stone", he called it *antimonium* (monk-killer).

This is one version explaining the origin of the name antimony. We shall not guarantee that the tale is authentic: the responsibility for it rests with the popular Czech writer Jaroslaw Hasek, who tells about it in his story *The Stone of Life.*

According to another version, this name which, as a matter of fact, is surviving in many languages, originates from the Greek *antos ammonos* — the flower of Ammon (a deity identified by Greeks with Zeus and by Romans with Jupiter). Growths of needle-like darkly lustrous crystals of the mineral antimonite really look like flowers. Some historians of chemistry believe that *antimonium* is derived from the Greek *antimonos,* enemy of seclusion, which illustrates the fact that antimony does not occur alone in nature but is always associated with other elements.

There are other versions, too. At any rate antimony is the name used by the famous Antoine Lavoisier when he drew up his list of known chemical elements. The Russian name for antimony is *surma* which comes



from the Turkish *surme* meaning rubbing or darkening of eyebrows. In early Russia the word surmit (to darken) was used even in the case of other diestuffs. At first surma referred to the purple-black antimony trisulphide and subsequently, to element No. 51. As for the Latin for antimony, *stibium*, it is judged to have derived either from the Greek *stibi* describing the natural crystalline mineral or from *stimmi* the name of a dye Greek women used for cosmetic purposes.

The history of antimony dates back to hoary antiquity. In the ancient kingdoms of the Orient (e. g. Babylonia) it was the material from which vases, goblets and other articles were made.

The first book giving a detailed description of the properties of antimony was *The Triumphal Car of Antimony* published in 1604, and its author, Basil Valentine, is mentioned in the history of chemistry as a German Benedictine monk. It has not been possible to establish the real person who went by that name, but it was proved early last century that the lists of monks belonging to the Order of St. Benedict had never included a Basil Valentine. According to one source, however, a monk named Basil lived in Erfurt Monastery in the 15th century and was claimed to be very well-versed in alchemy. Some of his manuscripts were found after his death in a box with gold powder, but he can hardly be identified with the author of the *Triumphal Car*. We must probably accept as correct the conclusion of a critical study of a number of Basil Valentine's books, according to which they were all written by different people and not earlier than the second half of the 16th century.

It was noticed even in medieval times that antimony was a difficult metal to forge compared to the "classic" metals and so it was isolated, along with zinc, bismuth and arsenic, into a separate group of "half-metals". There were also other reasons for such treatment of these elements: according to the laws of alchemy, every metal was associated in one way or another with a celestial body. "Metals were created seven — seven planets in the heaven", asserted one of the major postulates of alchemy. At one stage people really knew to more than seven metals and seven celestial bodies (the Sun, the Moon and five planets, not counting the Earth). It was believed that only ignoramuses could fail to see the profound philosophical truth contained in this fact. The theory of alchemy asserted that in the heavens gold was represented by the Sun, silver was doubtlessly the Moon, copper was related to Venus, iron had an affinity to Mars, mercury corresponded to the planet Mercury, tin embodied Jupiter and lead, Saturn. No room was left for any other metal.

While in the case of lead and bismuth such discrimination was clearly unjust, antimony with its peculiar physical and chemical properties indeed had no right to complain about being included among the "half-metals".

Judge for yourself. Although the main modification of antimony — crystalline or grey antimony — is a typical grey-white metal with a bluish tinge, which is the deeper the more impurities it contains (there are also three amorphous modifications: yellow, black and explosive antimony), it is firstly, exceedingly brittle and easily powedered, and second, a much poorer conductor of heat and electricity. In chemical reactions, too, its behaviour is such that it is impossible to give a definite answer to the question whether it is a metal or not.

As if in revenge for the unwillingness of other metals to accept it in their family, molten antimony dissolves almost all of them. This property was known even in old times and in many surviving alchemic books antimony and its compounds are depicted as a wolf with an open mouth. The treatise *Running Atlanta* by a German alchemist, Mayer, published in 1618 had a picture showing a king being devoured by a wolf. In the background, the same king, alive and well, was approaching a lake and a boat ready to take him across to the palace on the opposite bank. That was a symbolic depiction of the process of purification of gold (the king) from impurities of silver and copper by means of antimonite (the wolf), the native sulphide of antimony. When gold was melted with antimonite, silver and copper formed sulphides and gold combined with antimony. After that the compound was placed in a current of air causing antimony to volatilize in the form of trioxide, leaving pure gold behind. This process was practised up to the 18th century.

The content of antimony in the earth's crust is only $5 \cdot 10^5$ per cent. It is a component of about one hundred minerals, the most widespread of which is the mineral antimonite or stibnite, which contains over 70 per cent of antimony and is the basic raw material for its commercial production. Its other important minerals are kermesite, servantite and valentinite.

In several cases antimony was found in meteoritic matter, but not on the Sun where the presence of many elements has been established spectroscopically.

Considerable deposits of antimony-containing minerals occur in China, Czechoslovakia, Bolivia, Mexico, Japan, the United States and some African countries. In pre-revolutionary Russia there were no discovered deposits of antimony ores and no antimony was produced (at the beginning of the 20th century the country imported almost a thousand tons of antimony a year). Prominent Soviet geologist, Academician D. Shcherbakov, mentioned in his memoirs discovering signs of antimony ores in the Kadamjay Mountains in Kirghizia in 1914. But then the situation in Russia was such that the authorities had to deal with other priorities first. A geological survey was carried

out there twenty years later and already in 1934 the trisulphide of antimony began to be produced from the Kadamjay ores, and a year later, the first batch of national metallic antimony was produced. By 1936 no imported antimony was needed.

The process of extracting antimony from an ore or a concentrate is not too involved: roasted with iron, it is liberated from its sulphides and then reduced by carbon. There is also a hydrometallurgical process: antimony is transformed into a solution and then extracted electrolytically. But these processes have a significant shortcoming: the metal obtained is far from pure, the content of iron, copper, arsenic, sulphur and other elements in it sometimes reaching 10 to 15 per cent.

Few buyers can be satisfied with such a product, which means that crude antimony must be purified. Thus, it is melted once more with substances actively reacting with its impurities. Sulphur combines with iron, arsenic is liberated by sodium, and iron and copper are ousted by antimony sulphide. This process is called fire refining.

In the process of electrolytical extraction the current passed through the electrolyte in a large bath acts above all on the atoms of antimony depositing them on the cathode where they "cling" together. The current is indifferent to the impurities and they are left in the bath.

Refined antimony contains not more than 0.5 to 0.8 per cent of impurities. But even this cannot satisfy all consumers. For example, in the semiconductor industry 99.999-per-cent pure antimony is applied. Such purity is obtained by zone melting (the crystallophysical method). A bar of antimony in a graphite container (in the shape of a boat) is charged into a quartz tube, along which moves an annular electric heater. During melting first one section (zone) of the bar is heated, then another and so on. When the heater moves away from the heated zone the metal in the zone begins to solidify and all impurities travel to the next melted zone, owing to the physical law, according to which impurities cannot crystallize together with the base material but must remain in the liquid phase. (The ice-sheet covering the norhern seas in winter contains no salts, although sea water is fairly rich in salts). Moving along with the zone of the melted metal, all impurities finally collect at one end of the bar which is cut off and the rest of the antimony — now a super-pure product, is sent to the stock-room. In some special cases the melting takes place in an atmosphere of an inert gas (argon) which does not become involved in any reaction.

The metal obtained in a multi-stage purification process will satisfy the most demanding consumer. At a world fair held in Brussels in 1958 super-pure antimony produced by the Kadamjay integrated works was recognized as the best in the world and formally accepted as a world standard.

It is precisely this grade of antimony that is used as an alloying addition (only 0.000001 per cent) to germanium, one of the most important semiconductor materials, which greatly improves its properties. But if this addition contains even one atom of copper per thousand atoms of antimony it will only do harm to the metal. This is why antimony passes through the lengthy process described above before being sent to enterprises producing semiconductors. Some antimony compounds (e. g. with gallium and indium) are themselves excellent semiconductors. Many antimony-containing semiconductor materials were obtained in weightlessness on board the Soviet *Salyut-6* and the American *Skylab* space stations.

But the amount of antimony that goes into semiconductors is not large. The metal is mostly used for the making of alloys — about two hundred of them in all. Georg Agricola, an important 16th century metallurgist, wrote: "If a certain amount of antimony is melted with tin, it makes a metal from which the type used by book printers is manufactured." It is the same today: not a single printing shop can do without type metal (an alloy of lead with antimony and tin). Unlike other metals, melted antimony (also gallium and bismuth) expands in volume on solidification. This is why when the type is cast the metal containing antimony makes a tight filling in the matrix on solidification. Owing to this property, the mirror image of a letter, symbol, etc., to be printed turns out to be extremely accurate. Furthermore, antimony makes type metal hard and wear-resistant which is especially important, considering that each character block has to leave its impression on paper tens of thousands of times. The ability of cooling antimony to expand also explains the use of its alloys in ornamental castings where the reproduction of the finest details is essential.

Hard and corrosion-resistant alloys of lead and antimony are used in chemical engineering (as a lining of baths and other acid-resistant equipment), in tubes transporting acids, alkalis and other aggressive liquids; also for covering electric, telegraph and telephone wiring, grids of lead-acid plates, bullet cores, shot and shrapnel.

Along with tin and copper, antimony is used in bearing alloys (babbitts). The first such alloy was developed by the American engineer Babbitt in 1839. Despite their long history babbits still enjoy designers' respect. Their structure — hard particles in a soft base — imparts the bearings high antifrictional properties: a low friction coefficient, a smooth running-in, and a high resistance to galling. An addition of 0.5 per cent of antimony to pig iron makes another fairly good antifrictional material.

Of late years antimony has been used in crime detection. It appears that a bullet in flight creates an eddy flow in its wake which contains microscopic quantities of various substances, including lead, antimony, barium and copper. Settling on the ground, a floor or some other surface, they leave an invisible trace, that is, invisible to the unaided eye. Modern science makes it possible to see this trace, hence to establish the direction of the bullet's trajectory. Strips of wet filter paper are applied to the surface under examination, then placed into a nuclear reactor and subjected to neutron bombardment. As a result some atoms (atoms of antimony included) sticking to the paper become radioactive isotopes, the rate of whose activity is indicative of the content of corresponding elements in the samples. This enables researchers to deter-

mine the trajectory and distance of the bullet's flight, the characteristics of the bullet itself and the weapon from which it was fired.

Antimony compounds find wide applications as well: in vulcanization of rubber; for impregnation (antimony trioxide) of fabrics used for theatre curtains, drapes and tarpaulin to make them fire-resistant; in paints coating the submerged parts and super-structures of ships; antimony compounds are added as a pigment to many paints used in art ("Neapolitan yellow") in ceramics, chinaware and opal glass.

We often hold one of the antimony compounds in our hands: mixed with red phosphorus it covers the sides of match boxes (that is why they are dark brown). Some salts of antimony have good pyrotechnical characteristics. Antimony proper can also produce a beautiful firework display: if fine antimony powder is slowly poured into a vessel with chlorine its grains will flare up like bright starlets. The vessel will soon fill with the white smoke of antimony pentachloride. Explosive antimony is so unstable that it explodes on touch or on being heated even very slightly and transforms into ordinary grey antimony.

A discovery based on biochemical processes connected with bacteria was registered in the Soviet Union in 1974. Years of study of antimony deposits showed that antimony could gradually become oxidized although this does not happen under ordinary conditions (the process can take place at over 300°C). What makes antimony change its chemical behaviour in the deposits? Microscopic examinations of oxidized antimony revealed that it was "densely populated" with hitherto unknown bacteria which were responsible for oxidation. But that was not all. It appeared that on completing the process of oxidation the bacteria immediately used the resultant energy on chemosynthesis, that is, on the transformation of carbonic acid into organic substances.

The phenomenon of chemosynthesis was first discovered and described in 1887 by a Russian scientist, S. Vinogradsky. But until now science has known only four elements releasing energy for chemosynthesis during bacterial oxidation: nitrogen, sulphur, iron and hydrogen. And now antimony has been added to the list.

Cs

TWO BLUE STRANGERS (CESIUM)

Whims of history.— For truth's sake.— The flame changes its colour.— A symphony of colours.— The good prince.— Visiting cards.— A parcel from Schwarzwald.— Two blue lines.— Sherlock Holmes will not be interested.— You smoke cesium.— The jury award a prize.— How to keep it?— Not to be touched.— Not all like light.— A lonely electron.— A bribe for a mechanism.— For hundreds of miles ahead.— Seeing through the night.— On the way to distant stars.— Swollen atoms.— Today and tomorrow.

History is choosy. It is seldom one can find oneself mentioned in its best pages. In chemistry only those "individuals" are accorded this honour that were able somehow to outdo their competitors. It is logical in a way. Did not technetium have a right to a special place in history as the first artificially created element? Or helium, the only "resident" of the periodic table that was first discovered on the Sun and only after that, on our planet?

Among the fortunate ones we find cesium, an element which wrote its name in blue letters in the history of spectral analysis. But for truth's sake it must be said that not cesium but the German scientists Bunsen and Kirchhoff wrote this name in history. As to the colour of the letters in which it was written you will soon see that there was a good reason for it being blue.

In the 1850s Professor Bunsen of Heidelberg University was attracted by a phenomenon that seemed insignificant from the point of view of science: salts of metals put in a flame changed its colour. It is probable that this fact was noticed even before Bunsen, but it was this chemist that became seriously interested in the phenomenon and decided to study it. One after another he held grains of different substances over the burner and every time the flame changed its colour like a chameleon, turning violet, then yellow, then pink. Bunsen's experiments revealed two facts: first, every one of the "test metals" imparted a definite colour to the flame, and second, the colour did not depend on the state of the metal. All compounds of barium, for one, gave the flame a greenish tinge, while calcium made it red.

Was it possible to use this phenomenon to determine simply and quickly what elements a substance under study contained? That could signify a real revolution in chemical analysis. No doubt, the idea was extremely attractive, but hardly practicable. As a rule, a substance contains several components that can confuse the picture. When such a "company" finds itself in the fire it produces a whole symphony of colours. Moreover, some of the colours, say, the bright yellow of sodium, will be much more intensive than the rather inconspicuous pinkish-purplish of potassium. One colour will mix with another, while the tints and tinges will be lost against the background of more vivid colours. In such circumstances no analysis can be sufficiently accurate.

Did this mean that the idea had to be given up almost as soon as it was conceived? In fairy tales in hopeless situations there always comes a good prince or a fairy, everything changes for the better and a happy end is ensured. Something like that also happened at Heidelberg University. The role of the good prince was played by Bunsen's friend and colleague, Professor Kirchhoff, a physicist by then already well known for his works in optics. At that time Kirchhoff was studying the spectra of heated solids and liquids. He suggested to Bunsen that not the burner's flame but its spectrum, in which all the colours and tinges were seen much more clearly, should be studied. Taking two spy-glasses, glass prisms and a sigar box, Kirchhoff built a spectroscope-like device, which could split the flame, as it were, into its component parts. While before the flame was studied with the naked eye, now the scientists had a ray of light from the burner passing through several lenses and a prism and being transformed into a band of numerous vertical lines of different colours.

When Bunsen placed a crystal of table salt in the flame, Kirchhoff who was looking into the instrument, saw two bright yellow bands against a black background. No doubt, it was a visiting card of sodium. Other sodium compounds were placed in the flame after that — sodium carbonate, saltpetre, sodium sulphate — and invariably the two yellow lines emerged in one and the same region of the spectrum.

Days, weeks and months passed. Gradually hundreds of substances had passed through the flame, the prism and the spy-glasses. The two scientists became convinced that every element was characterized by its own spectral lines by which it could always be detected, just like a criminal was detected by his fingerprints. No component of a substance, even if measured in millionths parts of a milligram, could escape the magic eye of the spectroscope.

Bunsen and Kirchhoff carefully studied all the known chemical elements and drew up a precise spectral characteristic for every one of them. Their work signified the birth of spectral analysis, an entirely new method, which not only indicated the presence of an element in a substance, but also made it possible to establish the quantity of that element by the intensity of. its spectral lines. But that was not all.

One day, in 1860, Bunsen received a parcel at his laboratory with mineral water from the famous Schwarzwald springs. The local doctors asked him to determine its composition, so that they could explain its curative properties. Why not? Bunsen evaporated the water and placed a drop of the concentrated solution in the flame. Looking through the spectroscope his trained eye immediately detected the lines of sodium, potassium, calcium, strontium and lithium.

But there were two blue lines he could not place. Could it be strontium? But strontium showed only one line. Bunsen kept comparing the spectrum with all the known standards, but could find nothing that looked like it. Neither could Kirchhoff. This meant that a new chemical element was discovered. They gave it the name cesium (meaning in Latin sky-blue).

Thus, cesium was the first element which was not discovered chemically like dozens of its elder "brothers" but by a spectral analysis. As years passed, the spectroscope announced to the scientific world the birth of rubidium, thallium, indium, gallium and samarium, but it was cesium that went down into history as the first-born of spectral analysis.

A few years after it was discovered cesium shed light on one inexplicable incident. It concerned a loss which had for years baffled chemists in many countries, though it could hardly interest Sherlock Holmes or Inspector Maigret. In 1846 a German scientist, Plattner, set about studying pollucite, a mineral found on the Isle of Elba. To make a complete chemical analysis of the mineral was not difficult, but Plattner was puzzled by one circumstance: no matter how carefully he summed up his measurements of the component parts of the mineral, the total came to only 93 per cent. Where were 7 per cent missing? For almost twenty years the question remained unanswered. It was only as late as 1864 that the Italian scientist Pisani furnished irrefutable proof that it was cesium responsible for the loss. Plattner had mistook it for potassium. These two elements have many chemical properties in common, but cesium is almost twice as heavy.

Cesium is a scarce element but still its traces are found in many types of mountain rock and in sea water. As to its relations with mineral water, they have been mentioned earlier (although it is true that Bunsen had to evaporate 40 tons of it in order to obtain a few grams of cesium salts). Curiously, traces of cesium have been found

in sugar beet, coffee beans and tea leaf. Every tobacco smoker must also be familiar with it: there are two blue lines in the spectrum of tobacco ash.

If metals were given prizes for reactivity, a panel of most authoritative chemists would doubtlessly award it to cesium. Not only is it "the most metallic" of all the others in the periodic table (except francium the reserves of which in nature are practically zero), but also exceptionally active chemically. Once in the air, pure cesium ignites immediately and burns up; it reacts violently and explodes on contact with sulphur and phosphorus, let alone the "opponents" of all metals, the halogens; its association with water is also fraught with a "conflict situation": hydrogen liberated in the reaction also leads to an explosion and fire. Even ice, a chemically "peaceful" substance, cannot remain indifferent to cesium: cesium "clashes" with it furiously and will not be pacified even by a severe frost (up to minus 116°C).

Small wonder, therefore, that it is extremely difficult to obtain pure cesium. This problem was solved for the first time in 1882 by the Swedish chemist K. Setterberg who extracted it electrolytically. The process in use today was suggested in 1911 by the French chemist A. Axpille: cesium is forced out of its chloride by metallic calcium in a vacuum under a temperature of around 700° C.

But once obtained, how is one to go about storing pure cesium? You realize, of course, that this is not an idle question, but the answer to it is really paradoxical: it must be made impure, that is, melted with other metals. Cesium alloys are not aggressive and can keep as long as required, after which the pure metal can be extracted by distillation in a vacuum.

"Fresh" cesium is a lustrous metal with a pale golden tint. It is soft like wax and light like magnesium or beryllium. It is common knowledge that mercury is the lowest melting metal and in this respect it has no competitors. But of all the other metals, cesium is the easiest to melt: its melting point is 28.5°C. The warmth of the human palm is enough to do it, but we hope you will remember what we have told you about its "explosive nature" and will not try to do it.

It goes without saying that it is impossible to use cesium to make machine parts for operation under load, or in a hot furnace or in contact with chemical aggressors. Are we to assume then that this "touch-me-not" of "blue blood" is a good-for-nothing and presents no more than a purely scientific interest? Indeed, it cannot compete with iron, aluminium or titanium in practical use, but then it possesses unique properties, such that not a single other metal can boast. To describe this property we will have to make another digression into the last century.

In 1887 a well-known German physicist, Heinrich Hertz, discovered the phenomenon of photoeffect, that is, "evaporation" of electrons from a metal surface under the action of light. Soon after that A. G. Stoletov, Professor of Moscow University, carried out a series of experiments and formulated on their basis the theoretical laws of photoeffect. In substance, this phenomenon is based on the fact that the weightless ray of light carries sufficient energy to knock out an electron on the outermost orbit of an atom of some metals. If a flux of such liberated electrons is directed into a break in an electric circuit it is capable of closing it.

Different metals react differently to light, hence, do or do not emit electrons when irradiated by it. Some will not give up their electrons even if "bombarded" by a searchlight, others, on the contrary, readily abandon them as soon as hit even by a very dim ray. In this respect cesium is the most generous metal and there is a valid reason for it: all alkali metals (and cesium is their most typical representative) have only one electron travelling on their outer orbits, which is why this electron is easily dealt with by light. In the case of cesium, besides, this "wanderer" is situated farther from the nucleus than in the atoms of its alkali "relatives". Therefore, the "effort" required to knock out the outer electron is minimal in cesium, which means that it is the most suitable material for the photocells, that is, devices transforming light into electricity. In the photocells cesium is alloyed with antimony and the photosensitive layer of the alloy is so thin that one gram of it covers a surface of something like 10 sq metres.

We come across photocells in the underground stations every day. They are inside the turnstiles all passengers have to pass, and operate on a very simple principle: on one side there is a photocell and on the other, a source of light directed on the person passing through. If you try to cross the ray of light without dropping a five-kopeck piece into the slot, the photocell will activate the levers that will bar your way. But this "bribe" automatically switches off the mechanism and the photocell cannot "notice" you.

Photocells are very simple but very capable devices that can be taught many jobs. As soon as darkness descends on a city, a photocell will switch on the street-lamps; if a machine operator's hand reaches into a dangerous zone, it will immediately stop the machine; it can sort cigarettes, count machine parts passing by it on a conveyor belt, check the quality of polishing of bearing balls, and read the sound track on a film. It is a most reliable night guard at shops, banks and warehouses.

The very idea of transmitting visual images over distances would be inconceivable without the photocells. Whenever you have a chance to see a hockey match, a concert or an episode of a thriller, you must thank cesium for it. Without it your TV set would have no more meaning than an empty box.

It is also photocells that are responsible for photographing the reverse side of the Moon. Without the "light-loving" electrons it would have been impossible to transmit by telegraph such things as drawings, charts, photographs, letters, etc.

Based on the photoelectric properties of cesium is the introscope, a device making it possible to take a look inside opaque objects for possible flaws. Cesium is also sensitive to infrared radiation, hence its use in optical instruments that can "see" at night — a fine aid to drivers — and in telescopic sights.

Something akin to photoelectric effect also takes place under the action of heat on cesium. This is why this metal is more readily transformed into ionized gas or plasma than most other chemical elements. Cesium plasma is of enormous theoretical and practical interest. For instance, in outer space where the extent of rarefaction is very high a flux of electrons emitted by atoms of cesium is capable of creating a jet thrust so powerful that it can impart colossal speed to rockets (according to Western specialists it can be up to 44 km per second!). Perhaps the hour is not so far off when rockets working on cesium fuel will be reaching the remotest points in the Universe.

Right now, though, cesium plasma has enough to do here on earth. In magnetohydrodynamic generators it transforms heat into elecricity. One of this generator's many advantages is that it is simple in design: the only moving part is ionized gas which plays the role of rotor. Cesium is likewise indispensable to thermionic energy converters, also transforming heat energy of the nuclear reactor into electricity. The first-ever installation of this type, *Topaz*, has been commissioned in the Soviet Union.

Cesium is the object of intensive scientific research. Several years ago physicists at Bielefeld University in Western Germany carried out an interesting experiment. It lasted a tenth of a second and took two years of preparations. What was it? An atom of cesium placed in a special installation was subjected to bombardment by an impulse of a powerful laser. As a result the atom got into a state of such great excitation that its electron orbits stretched and it grew in size tens of thousands of times.

A group of American physicists at Oak Ridge (one of the biggest atomic industry centres in the USA) has developed a method of counting up, one by one, the atoms of some elements, which is also based on excitation of atoms by powerful laser impulses. Cesium was the first element used for the demonstration of the new method.

Scientists at the Indian Institute of Geophysical Research, who studied the water from 60 hot springs in the Himalayas, drew the conclusion that a higher concentration of cesium in water could be a sign of volcanic activity. A high concentration of the isotope cesium-137 has been detected in trees surviving in the region of the famous Tunguska explosion in Siberia, and the most interesting fact is that this chemical anomaly is observed exactly in the layers of the trunks formed in 1908 when the event took place.

There is another interesting fact associated with cesium. In 1967 the International General Conference on Weights and Measures established that "One second is a time defined as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between two hyperfine levels of the ground state of the cesium-133." Yes, simple as that! You want to measure one second? Just wait for an electron of cesium to jump from one of its orbits to another a definite number of times. If a human being will find this job rather hard, atomic timepieces already operate on the basis of this time unit and quite efficiently. Their accuracy is such that in three millennia from now they can be at fault only one second either way. This is to be explained by the extraordinary stability of the main properties of cesium atoms.

But for reasons of space, we could go on telling about cesium indefinitely. We could tell about its catalytic properties and its ability to create a vacuum in electron tubes, about its isotopes used in medicine, flaw detection, and measuring instruments, about its part in producing scintillating single crystals that become alight with a cold bluish or greenish glow under the action of any radiation. Its range of application is vast, but its future is really boundless.

Ba

THE GOOD LUCK OF A SHOEMAKER FROM BOLOGNA (BARIUM)

The Bologna gem.— Heavy or light?— Experiments in a carbon crucible.— Hot-tempered.— Illegal activity.— The evil must be exposed.— In banknotes and bonds.— A light breakfast.— Mysterious rays.— Replacing fish scales.— The green of fireworks.— The Sphinx is given injections.— Unmatched.— Who is right?— Salt in the flame.— Are there any vacancies?— Crystals change their colour.— Errors are instructive.— With utmost precision.— In a magnetic field.— A pharmacist's discovery.— Outstanding ability.— What is in the way?— The sky over Columbia.

The history of this element goes back to the Middle Ages and the peak of alchemy. In 1602 Casciorolus, a shoemaker and alchemist from Bologna, found a stone in the local mountains which was so heavy that it would be only too ridiculous not to guess that it contained gold. So thought the shoemaker as he carried the stone to his shop where he was going to get gold from it immediately.

First he decided to roast the stone with coal and drying oil. Although no gold was produced, the experiment was promising: on cooling the stone shone in darkness with a reddish glow.

Being a sociable man, Casciorolus did not conceal the secret of the stone from his colleagues, the alchemists, and the whole of the gold-seeking crowd was brought into a state of great agitation. The shoemaker's mineral, which began to be called the "sun stone", "Bologna stone" or "Bologna gem" became the principal participant in numerous reactions and experiments. But as no gold was obtained, the interest in the new mineral died down gradually.

It was a hundred and fifty years later, in 1774, that the well-known Swedish chemists Scheele and Hahn carefully studied the "Bologna stone" and found it to contain a peculiar "heavy earth", which was first called barot, then barite (from the Greek *barus*, heavy), and the metal that formed the "heavy earth", was called barium.

In 1808 Sir Davy of Britain isolated metallic barium electrolytically from barite. Since it turned out to be rather light (its density is 3.7 g/cu cm) another British chemist, Clarke, suggested that the name barium should be changed into plutonium in honour of the mythical lord of the Hades. He was not supported, however, and the light metal continued to be called "heavy". It will be noted that according to modern technical classification barium is really referred to as the heaviest in the group of ... light metals.

Today metallic barium — a soft white metal — is obtained by aluminothermic reduction of its oxide. This process was first developed by the Russian physicochemist Nikolai Beketov, who became the founder of aluminothermy. This is how he described his experiments: "I took some anhydrous oxide of barium, and adding to it a quantity of barium chloride as a fusing agent and alumina, placed the mixture in a carbon crucible and roasted it for several hours. When the crucible cooled down I found in it a metal alloy looking entirely different from alumina and having different physical characteristics. This alloy has a macrocrystalline structure, is very brittle, and shows a yellowish, mildly lustrous surface in a fresh break. A quantitative analysis has shown that to 100 parts of the alloy there were 33.3 parts of barium and 66.7 of alumina, in other words, two parts of alumina to one part of barium..."

Today this process is carried out in a vacuum, under a temperature of 1 100 to 1 200° C. Along with the reduction of barium oxide by aluminium there also takes place the process of distillation of reduced barium which is then condensed in its pure form.

Barium is a very active chemical element. It ignites readily on heating or under an impact, readily reacts with oxygen (on exposure the lustrous surface of fresh barium soon covers with an oxide film), nitrogen, hydrogen and water which is why, like other "hot-tempered" metals, it is kept immersed in kerosene. This explains the rather limited uses of metallic barium. Its main "occupation" is that of absorber of residual gases, or getter, in high vacuum technology. Small quantities of this metal are used in the metallurgy of copper and lead as a deoxidizer and a sulphur and gas removing agent. Some barium is added to bearing and type metals, the main component of which, lead, becomes much stronger with even small additions of it. The electrodes for spark plugs in engines and radio electron-tube components are made from an alloy of barium with nickel.

Barium compounds have a much more extensive application. Barium sulphate, or heavy spar, has long been associated with the production of paints. True, it must be said that at first the use of barium sulphate in this field was illegal: ground spar was mixed with white lead making it much cheaper though poorer in quality. Owners of paint factories made handsome profits by shamelessly selling their erzats for almost the same price.

In 1859 the Russian Manufactures and Home Trade Department received a report concerning underhand operations of Yaroslavl (a port on the river Volga — *Ed.*) manufacturers who mixed white lead with heavy spar, "which deceives buyers as to the quality of the goods", and also a request "to forbid the above manufacturers to use spar for the production of white lead." A report to the same effect was later delivered to the Minister of Finance "who as we hear, has instructed Yaroslavl authorities to carry out an investigation. But since the matter was put in charge of the chief of police Krasovsky, the main protector of the manufacturers, the result was, naturally, that the manufacturers repented in his office after which they became even more impudent in concocting their products." The report asked "to expose the same evil at the fair in Nizhni Novgorod (today Gorky — *Ed.*), from where the paint is taken away in all directions, to the very borders of the Empire. It is very easy to expose it, it is only necessary to ask all the manufacturers of the white paint why they send out orders for such great quantities of spar, what they use it for, and if they use it in the white lead, what are the results of this operation".

All those petitions, however, remained unheeded. Furthermore, in 1882 a spar works was commissioned in Yaroslavl which turned out, in 1885, 50 000 poods (800 tons — *Ed.*) of ground spar for the same purposes. In early 1890s Mendeleyev wrote: "...Barite is added to white lead at many factories since the paint imported from abroad also contains it which reduces its price."

Gradually barium sulphate won a legitimate place in the paint industry: it began to be included in lithopone, a white paint with a very good hiding power, much liked by customers. It is also used as a weighting and filling agent in the production of some types of high quality paper (for paper money, bonds, documents). A suspension of this salt in water is used as a flush-fluid in drilling deep oil and gas wells. Barium sulphate is opaque to X-rays, much more so than the tissues of the human organism. This quality is the basis of diagnosing gastrointestinal diseases. The patient is given "barium meal"

(barium sulphate mixed with cooked semolina or water) and then his stomach is x-rayed: the opaque mass produces a clear image of the stomach and intestines which enables a physician to spot any disorder. Its capacity to absorb X- and gamma-rays explains the application of barium sulphate in X-ray apparatus and nuclear reactors as a shielding material.

It will be recalled that the discovery of X-radiation is associated with another barium salt — barium platinocyanide. In 1895 the outstanding German physicist Wilhelm Konrad Roentgen concluded that this salt owed its green glow in darkness to the action of a hitherto unknown radiation. Wishing to underline its mysterious nature, Roentgen called the new radiation X-radiation, but soon the name Roentgen rays began to be used in many countries in honour of the discoverer.

We all admire the iridescence of pearls. Small wonder that the search for a way to produce pearl-coloured materials artificially has been going on since time immemorial. In old days this was achieved by using a fish-scale brew. Even now a pearl pigment is produced in this (though much improved) way in some places. But in our age of chemistry it is absurd to rely on fish scales and so, they have been effectively replaced by barium thiosulphate. Crystals of this substance mixed with some colourless varnish make it pearly. If the same crystals are introduced into gelatin or joiner's glue, the imitation mother-of-pearl will be perfect.

Glass manufacturers are well familiar with barium carbonate which is added to the glass mixture in order to improve its refractive coefficient. Sometimes barium nitrate is added for the same purpose. But the "favourite job" of the nitrate is fireworks. The bright green colour of this salt and also of barium chlorate, is indispensable in all firework displays. Barium chlorate, besides, is a very good weed-killer greatly respected by farmers.

The Great Sphinx, the guardian of the Egyptian pyramids, has kept its vigil for almost five millennia now. Hewn from an outcrop of a lime rock at the order of King Chephren, it has the body of a lion and a human head which is said to be a portrait of Chephren himself. Even if the pharaoh's face shone with beauty in long-gone days, right now his gigantic copy has lost all attractiveness: the sand storms and rains and the sharp drops in temperature have practically wholly destroyed its nose, given a noticeable squint to its left eye and lined its face with deep furrows. The statue's neck is especially vulnerable as it is constantly "losing weight" and becomes thinner. A Cairo newspaper wrote that "the Sphinx is sick and unless urgent measures are taken the neck may break". Several years ago attempts were made to "cure" it: it was given "injections" of barium salts that were to strengthen the parts threatening to collapse. That helped, but not for long, and four years later the Great Sphinx had to be "closed down" for major repairs.

Barium oxide has a fairly long "work record". Almost to the end of the last century it was used to produce oxygen. For that it was roasted under a temperature of 500-600° C during which it absorbed oxygen from the air and transformed into barium peroxide; when the temperature of the process was raised to 700° C, the peroxide again transformed into the oxide, giving up the excess of oxygen. This process was used until the method of extracting it from liquid air was developed.

Another interesting page in the history of barium oxide was written in 1903 by a German physicist Wehnelt. And what happened was by pure chance. One day Wehnelt was instructed to verify, by means of a platinum wire, the law of emission of electrons by heated bodies which had been discovered by a British physicist Richardson not long before. His very first experiment confirmed the law and next day Wehnelt decided to repeat it with another wire. To his great astonishment he saw that the new wire was emitting an electron flux much more powerful than the day before: the instrument measuring the flux had almost broken down. Since the properties of the metal could not have changed so dramatically, the scientist had to suppose that the "electron storm" had been caused by a substance which had got on platinum by chance and had a much greater emissivity. What could that substance be?

Wehnelt began to deposit one substance after another on the platinum wire, but immediately saw that not one of them could have any influence on the electron flux. When he was ready to give up, he suddenly remembered that the lubricant used in the pump that was "taking part" in the experiment contained barium oxide which could well get on the platinum wire. He switched on his instruments once more and only moments later was overcome with joy: he had discovered a substance that had no equals in the capacity to emit electrons when heated.

True it was not immediately that the scientific world supported Wehnelt's conclusion. After the scientist had published the results of his experiments many physicists started their own experiments to check his results. One after another they reported that Wehnelt had greatly exaggerated the emissive capacity of the oxide of barium. Wehnelt himself failed to confirm his discovery by further experiments and, disenchanted, soon stopped them altogether.

It was almost twenty-five years later that an English physicist Coller became interested in the oxide. He staged a series of more sophisticated experiments and found that if barium oxide was heated in a vacuum under very low oxygen pressure, its electron emission would be very high. If the pressure of oxygen was increased during heating, the intensity of the emission dropped sharply. On the one hand, his conclusion restored Wehnelt's scientific reputation, but on the other, coincided with the opinion of his opponents. Since the oxide of barium did not change either in its chemical composition or crystalline structure, there was a new mystery to be explained: why one and the same substance behaved so differently, while not changing chemically?

Meanwhile a German physicist, Paul, discovered some abnormalities in the behaviour of a number of other simple substances and thus confused the issue still more. First, he put some common table salt (sodium chloride) in the flame. On evaporation of sodium the crystals became purple. The same happened when he tested potassium chloride: in potassium vapour the substance became dark blue. But judging by the experiments with barium oxide, these substances were not to have undergone any chemical change.

But was it really the case? It was found that some change did take place. The meaning of the mysterious phenomenon was explained in 1935 by Paul himself. He advanced a theory according to which a crystalline substance was characterized not by a permanent relation between atoms of different types but by a permanent relation between the sites of its lattice. In sodium chloride, for one, some sites belong to the cations (positively charged ions) of sodium and others, to anions (negatively charged ions) of chlorine. Each pair of the sites form as it were, a "two-room" apartment which does not necessarily have any "tenants". If the relation between the different ions in the crystals does not correspond to the stoichiometric relation typical of the given substance (such crystals were subsequently termed non-stoichiometric), its properties may change.

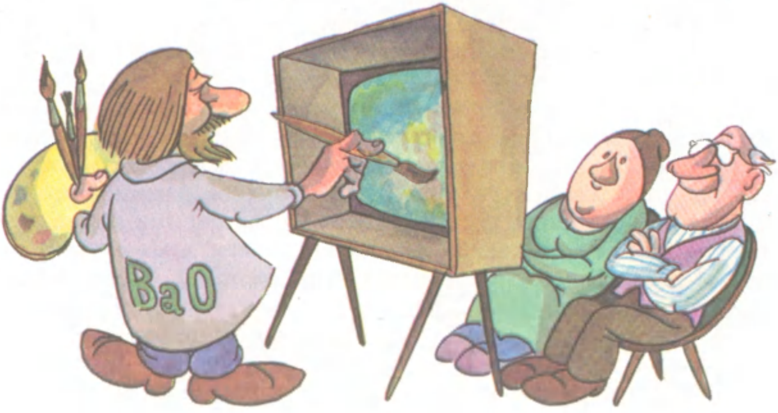
Paul reasonably supposed that when sodium chloride is heated atoms of sodium vapour may get onto the surface of the crystals of sodium chloride. In the process each of the atoms gives up an electron, becomes a cation and builds itself a "room" (lattice site). There it is immediately joined by an anion of chlorine which abandons its former site in the crystal and becomes the future "neighbour" in the new "two-room" apartment. The vacancy left by the anion of chlorine is at first occupied by an electron liberated by an atom of sodium. But it would not be in the nature of the electrons to stay "indoors" for a long time. In order to break out of its "confinement" the electron must be imparted energy equal to a quantum of yellow light. The non-stoichiometric crystals of table salt, possessing an excess of sodium, absorb yellow light and, in accordance with the laws of the spectrum, assume a purple colour. Careful measurements provided an answer to the question as to how many excess atoms of sodium would be required for the change in colour (it was established that the number corresponded to only a few thousandths of one per cent).

But back to barium oxide. In 1953 an American physicist, Sprawl, heated some colourless crystals of this substance in liquid barium and they turned red. The scientist assumed that the same changes as in table salt had taken place, the only difference being that in the former case the vacancy in monovalent chlorine was filled by one electron and in the latter, the vacancy in bi-valent oxygen was filled by two electrons. That was what explained, to his mind, the great emissivity of electrons. In other words, the vacancy in oxygen became the natural source of electron emission. The appeal of this hypothesis lay in its simplicity. What remained to be done now was to carry out some measurements to see that the electron flux directly depended on the quantity of excess barium in the crystals. But there was another setback in store: the experiments carried out in the laboratory of the Bell Telephone firm seemed to have completely refuted Sprawl's hypothesis.

It took another 15 years of painstaking effort to unravel the mystery. At the end of the 1950s the Soviet chemists, A. Bundel and P. Kovtun, suggested that the Bell Telephone experimenters had employed a faulty method: the thin layer of barium oxide, which was deposited on a metal base to determine the excess of barium, was not enough for an accurate chemical analysis. Apart from that, during the heating the layer could have become contaminated with admixtures from the base metal which would naturally distort the picture. But errors are instructive.

To avoid any more miscalculations, Bundel and Kovtun carried out their experiment with the most pure barium oxide, while contamination with admixtures was prevented by heating it in a special chemically stable material. The method and technique of the experiment was improved year by year, but the task was so difficult that it was only recently that the scientists were able to put the dots over all the i's: it was precisely the infinitesimal quantities of excess barium, measured with utmost accuracy, that were responsible for the electron emission. Thus, Sprawl's theory was fully confirmed, explaining the phenomenon discovered as early as the beginning of the century. It will be recalled in passing that the television picture is "drawn" by the flux of electrons breaking out of the non-stoichiometric crystals of barium.

Of late the oxide of barium has been used for the manufacture of ceramic magnets. This is achieved by placing the powders of barium oxide and iron in a strong magnetic field under pressure. The ferrate of barium that is formed in the process is characterized by peculiar



magnetic properties and is used in industry on an increasing scale.

Today, however, it is barium titanate, which is an excellent ferroelectric that is rightly considered the most important compound of barium. Ferroelectrics (or dielectric materials) are a special, fairly recently discovered class of chemical substances. Their history really began in the middle of the 17th century when a French pharmacist, Siegnette, discovered potassium sodium tartarate (Siegnette salt or Rochelle salt) which soon won a reputation of a good laxative. As such it was used for two and a half centuries, until in 1918 an American chemist, D. Anderson, found that within the temperature range from minus 15 to plus 22° C, Siegnette salt was characterized by a rather high dielectric permittivity and remained polarized even in the absence of external electric fields.

In 1944 a Soviet physicist, Vul, discovered that barium tetanate possessed considerable dielectric properties within a vast temperature range — from almost absolute zero to plus 125° C. Since barium titanate is characterized by great mechanical strength and is rather easily obtainable, it came to be considered one of the best ferroelectrics and a fine material for capacitors. Owing to their conspicuous piezoelectric properties (changes in electric characteristics under pressure), barium titanate is used in piezoelectric elements.

In our age of breathtaking technological progress the range of chemical elements claiming "responsible jobs" in science, industry, agriculture and other fields is ever increasing. However, many of them can hardly be used owing to their scarcity in the earth's crust. Barium is luckier than others, though: the crust contains 0.05 per cent of it which is several times more than nickel, cobalt, zinc and lead put together. It is really for the scientists now to find new interesting roles for it.

One of them is the manufacture of artificial comets. Fired from on board a spaceship at a great distance from the Earth, barium vapours become a dazzling plasma cloud which enables scientists to carry out various studies and optical observations, and to verify the trajectories of spacecraft. An artificial comet of this kind was first tested in 1959 during the flight of the Soviet *Luna-1* automatic station. At the break of the 1970s West German and American physicists, engaged in joint research into the Earth's electric and magnetic fields, dropped about 15 kilograms of the finest particles of barium at a very great altitude over Columbia, after which a plasma cloud was formed. Observed from different parts of America, the cloud stretched out along the magnetic lines of the globe which enabled the scientists to check the position of their craft in space. In 1979 jets of barium were fired from the Swedish testing ground at Kiruna. Under the action of the sun rays barium became readily ionized and created a glow which could be seen at great distances by means of supersensitive TV installations. The barium cloud was to shed light on some processes associated with northern lights, while its movement was to contribute to the knowledge of the nature of electric fields it came across.

As to the future of this element, it really promises to be fascinating.

Hf

ONLY A TRACE (HAFNIUM)

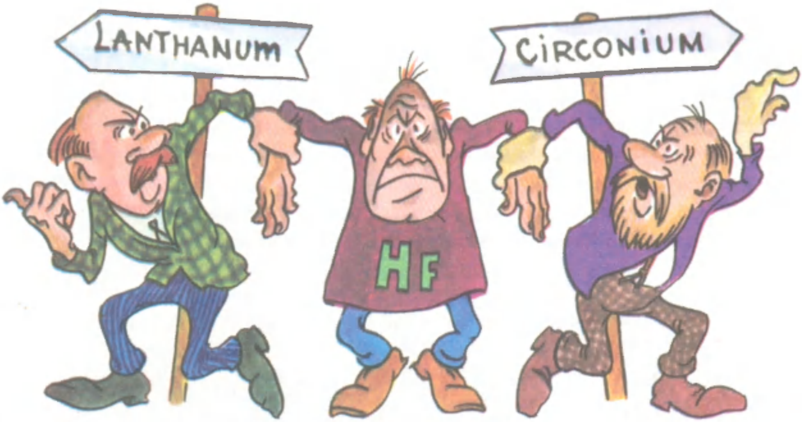
Who was lucky?— A mineral from Svyatoi Nos — Soap bubbles.— Heated arguments.— In honour of an ancient tribe.— Moseley's discovery.— Weighing in the balance.— In support of fellow-countrymen.— Not destined to be "asium".— Where are the traces?— A few words about twins.— A spoke in the wheel.— Threatened by hafnium.— Different views of neutrons.— No longer a by-product.— Reactor or an atomic bomb?— Worth its weight in gold.— Wonderful resins.— Needed by many.— Sapphire or fianite?—

Even a cursory glance at the periodic table is enough to notice the "geographical" nature of the names of some elements. Many of them reveal their association with cities, countries and continents. But not all place-names, naturally, have been credited with such honour. Of all the continents only Europe and America have their "namesakes" among the chemical elements, and Asia, among the rest, has not been as lucky. But at one time it was quite close to success, as you will see from the events described below.

Not long before the First World War a worker of the St. Petersburg Mineralogical Laboratory brought a sample of the mineral orthite from the Svyatoi Nos peninsula on the Asian shores of the Arctic Ocean. At that time many scientists were interested in radioactivity, and since there were reasons to believe that orthite contained thorium — one of the most interesting radioactive elements — it was decided to analyze the mineral chemically. Academician Vernadsky, the outstanding geochemist who headed the Mineralogical Laboratory, entrusted the job to his pupil, Konstantin Nenadkevich. Soon Nenadkevich succeeded in isolating grains of what could be expected to be thorium, but he was not sure about it.

Advised by Vernadsky, Nenadkevich determined the element's atomic weight: it was a little more than 178. That meant that in accordance with the periodic law the isolated element had to occupy a place between lutecium and tantalum, that is, square No. 72, which was still vacant at the time. Nenadkevich informed Vernadsky of the discovery of a new element.

Great as his desire to announce the discovery to the scientific world was, Vernadsky deemed it necessary to warn his excited pupil: "Do not hurry, the results must be checked and rechecked a hundred times before you anounce them." But then asked: "Where is it from?" "From Svyatoi Nos." "This means, from Asia. We'll call it asium."



But evidently, the biggest continent on the globe was not destined to be a relative of a chemical element. The First World War that broke out soon after, followed by the 1917 revolution and the Civil War put off the study of the new element indefinitely. Meanwhile other events having a direct bearing on the history of the new element took place.

When Mendeleyev "settled" all the known chemical elements in his table, square No. 72 remained unoccupied. The scientist could only suppose then that the atomic weight of the future tenant should be close to 180, while owing to the fact that its place was below zirconium, it should have common properties with this element and in nature should occur in association with it.

That zirconium ores contained an unknown admixture had been noticed a long time before. In the 19th century there were quite a few reports asserting that a new element had been discovered in the minerals of zirconium. The element was then "rediscovered" many times and each time was given a new name (ostranium, norium, jargonium, nigrium, euxenium) by which it lived not much longer that a soap bubble: every time careful analyses proved the fallacy of the "discoverers".

Drawing any definite conclusions concerning the identity of No. 72 was made extremely difficult by the fact that neighbouring it on the left in the elements table was the family of rare earths "headed" by lanthanum. At that time no one knew how many rare earths there were in nature and No. 72 became the subject of heated debate. Some scientists continued to believe that it should be chemically related to zirconium, others argued that it should belong to rare earths.

In 1895 Julius Thomsen of Denmark advanced a theory confirming the first point of view, but could not satisfy his opponents. At the beginning of the 20th century the French chemist Urbain became quite well known for his important contribution to the study of rare-earth elements. But in the case of No. 72 his views gave rise to much confusion.

In 1907 Urbain discovered lutecium (No. 71), the last element on the right in the row of the lanthanides. Urbain himself believed that after lutecium another rare-earth element would be found, and in 1911 he announced his discovery of this element. He thought it to be the last representative of the lanthanides which should be placed in square 72, and called it celtium in honour of the Celts, a tribe that had once lived on the territory of France.

Two years later a young British physicist, Henry Moseley, made an extremely important discovery: he established that the charge of the atomic nucleus, that is, the index number of an element, could be determined on the basis of its X-ray spectrum. His examination of the X-ray spectrum of a sample of celtium did not reveal the lines which element No. 72 should have produced. Moseley's conclusion was that Urbain's element was a mixture of known rare earths.

But Urbain was not willing to reconcile himself to the loss of celtium and countered that the results of Moseley's experiments were inaccurate owing to his imperfect instruments. But Henry Moseley could not give a reply to his French colleague: in the autumn of 1915 he, a member of the British expeditionary corps, was killed in action at Gallipoli, a city on the western shore of the Dardanelles. Meanwhile, A. Dauvillier, another French physicist who carefully studied celtium at Urbain's request, discovered two hardly discernible lines of element No. 72 in the spectrum of a mixture of lanthanides, thereby "rehabilitating" celtium.

But Urbain's joy was short-lived and for this he had to "thank" the celebrated Danish physicist, Niels Bohr. By that time Bohr's electron theory of structure of the atom made it perfectly possible to create the model of an atom of any element. According to this theory, the atom of element No. 72 could not have anything in common with the atoms of rare earths, but on the contrary, should resemble atoms of the 4th-group elements, titanium and zirconium.

Thus, weighing in the balance, were Urbain's experiments and arguments supported by Dauvillier's experiment on the one hand, and on the other, Mendeleyev's opinion, Thomsen's arguments and Bohr's calculations, as yet unsupported experimentally. Who was right?

Soon the answer was provided by the Hungarian chemist, G. von Hevesy and the Dutch physicist D. Coster. Never doubting Bohr's authority, they set about detecting element No. 72 in zirconium minerals. In 1923 they found the new element in Norwegian zirconium ores and their X-ray spectroscopic analysis showed that the charge of its atomic nucleus was 72. As to its chemical properties, they were close to zirconium, just as had been supposed by Mendeleyev, Thomsen and Bohr. Since the scientific argumentation of the discovery was faultless, the new element was placed in the periodic table. Hevesy and Coster gave it the name hafnium in commemoration of Hafnia, the old Latin name of Copenhagen, where the discovery was made.

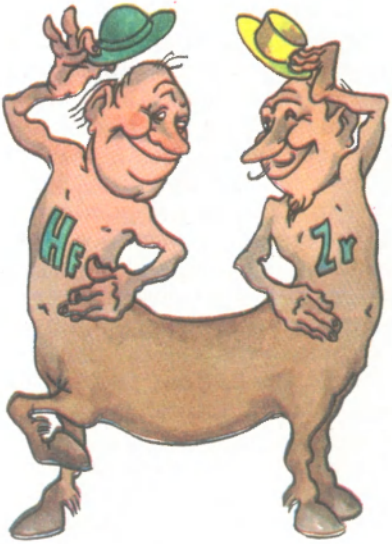
Although the fallacy of Urbain's and Dauvillier's view was beyond any doubt and celtium was from then on to be only a page in the history of chemistry, French scientists continued to call element No. 72 celtium for another 25 years in support of their fellow-countrymen. It was only in 1949 that the 15th Conference of the International Union of Pure and Applied Chemistry ruled that the element be referred to as hafnium and not celtium.

Thus, the balance was turned in favour of theory: Mendeleyev's periodic law and Bohr's electron model of the atom. But what then were the two lines Dauvillier had detected in the spectrum of a compound of lanthanides? Could it be that he compromised with his conscience in order to prove Urbain's faulty view? Not at all. Dauvillier had really seen those lines and they really belonged to element No. 72, for it is a fact that sometimes hafnium is found occurring in association with rare-earth metals which was true in this case and which had thrown the scientists off.

But what about the researchers in St. Petersburg? You have probably guessed by now that the element, traces of which were discovered by Vernadsky and Nenadkevich, was none other than hafnium, but since circumstances had prevented them from making their discovery official, the element was not called in honour of Asia, as Vernadsky had suggested, but in honour of the Danish capital.

What is this confusing element like? We can hardly suppose that you have had an opportunity of actually holding this silvery lustrous metal on your palm. It must be stated at the same time that its natural reserves are not at all scanty: they are 25 times greater than those of silver and 1 000 times greater than the reserves of gold. Yet, while all of you have seen silver and gold, it is doubtful that you have seen hafnium. What can explain this paradox?

It is the fact that it is greatly scattered and only traces of it can be detected. In fact, it is so thinly dispersed that there is not a single deposit of this element on earth. Like a shadow, it follows zirconium: any zirconium mineral contains traces of hafnium. But it is only zircon, in which there is only one atom of hafnium per 100 atoms of zirconium, that can be used commercially as a hafnium raw material. But between the raw material and metallic hafnium there lies an extremely complicated technological process. And it is exactly zirconium that makes it so complicated.



The point is that hafnium and zirconium are "chemical twins", and it is owing to this that zirconium was discovered almost 150 years earlier than hafnium. It is seldom that a pair of elements can demonstrate such great similarity in their chemi-

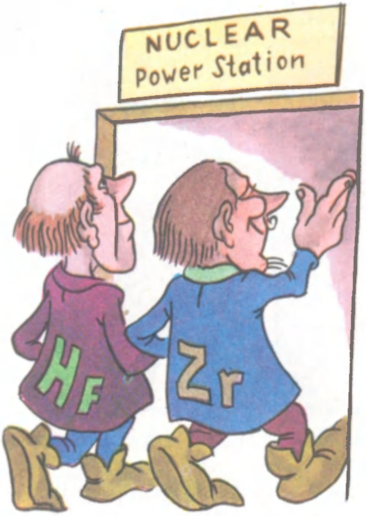
NEUTRONS ONLY

cal properties. It has yet been impossible to find a chemical reaction in which only one of the "twins" would take part and the other would not.

This incredible similarity is really a "spike in the wheel" of technologists attempting to separate the twins. In a recent past to separate hafnium from zirconium it was necessary to carry out 500 dissolutions and crystallizations, based on the literally microscopic difference in the solubility of the salts of these elements. The cost of this procedure can easily be imagined. This is why only 15 years ago or so there was no commercial production of hafnium and the few kilograms a year that were turned out were quite enough for purposes of research. As for zirconium which always contained traces of hafnium, it was not considered the worse for it.

Indeed, hafnium did not interfere with its more authoritative relative for quite a while. Zirconium was used generally as a corrosion-resistant material and since hafnium is also corrosion-resistant, it did no harm. As technology developed, however, and zirconium began to be used for the sheathing of uranium fuel rods in nuclear reactors, its association with hafnium began to be considered almost fatal. This is due to the fact that despite all their similarity, they have an entirely different attitude to neutrons. While zirconium is practically transparent to them, hafnium absorbs them avidly. The sheathing of uranium fuel rods must not slow down the neutrons and pure zirconium is the best material for it. But the presence of even two per cent of hafnium brings the neutron transparency of zirconium down to a twentieth of the value characterizing pure zirconium.

Scientists had seriously to concentrate on obtaining reactor-pure zirconium, that is, a metal containing not more than 0.01 per cent of hafnium. Five hundred operations were, naturally, out of the question from the point of view of industry, and scientists developed a process which was effective and economical enough. Hafnium, which was separated in the form of hydroxide, was first considered a by-product.



But soon that view changed radically: hafnium itself was found a job in the nuclear reactor.

As mentioned earlier, no nuclear reactor can function without the nuclear-opaque control rods regulating the rate of the nuclear reaction. When the rods have been removed from the reactor core the neutrons breed faster and faster, and without the control rods being introduced back into the core to absorb excess neutrons, the reactor could become an atomic bomb with all the ensuing consequences. It has been found that there is no better material for the control rods than hafnium with its excellent mechanical strength combined with great corrosion- and heat-resistance.

While at the beginning of the 1950s less than 50 kilograms of hafnium was produced in the United States, some ten years later the figure was 60 tons and the question of producing super-pure hafnium without any admixture of zirconium preventing its application in the atomic industry was high on the list of priorities.

Like most other new materials, hafnium is still very expensive. According to American estimates, hafnium rolled stock costs several times more than silver. On the one hand, this limits its uses and on the other, places the demand on chemists and metallurgists to develop such processes of its production that would sharply reduce its cost.

Very promising in this respect are ion-exchange resins. If a solution of zirconium and hafnium is passed through an ion-exchange column, the solution will be free from hafnium which will be "captured" by the resins in the column. Further treatment of the resins with acid will yield pure hafnium.

Hafnium is expected to find various applications in many fields of technology. Metallurgists, for example, believe that it can greatly improve mechanical characteristics of other metals and contribute to the development of new processes for the production of special heat-resistant steels. Hafnium's refractoriness (its melting point is above 2 200° C!) combined with its ability to absorb and liberate heat makes it a good structural material for parts of jet engines (blades, valves, nozzles, etc.). True, as such it has a significant drawback: it is twice as heavy as zirconium, three times heavier than titanium and incomparably heavier than beryllium. Hafnium may be found good for chemical engineering where it does not matter much whether it is heavy or light but where its corrosion-resistance may be extremely valuable.

In electrical engineering and radio industry hafnium is used for the manufacture of electron tubes and X-ray and picture tubes. Additions of hafnium dioxide to tungsten dramatically increase the life of filaments. The other hafnium compounds, the nitride and particularly carbide of hafnium (melting point 4 000° C) will doubtlessly win the reputation of especially important refractory materials.

A few years ago a new word — fianite (from the Russian abbreviation FIAN meaning the Institute of Physics of the USSR Academy of Sciences) — began to be mentioned quite often in the media. This word refers to the latest synthetic precious stones — single crystals of the dioxides of zirconium and hafnium. Displaying a superb play of colours (additions of various elements give practically any colour to the crystals) makes fianites every bit as beautiful as sapphires, topazes, aquamarines, garnets and other stones. But beauty is not the main advantage of fianites. Even more important is the fact that they are characterized by many unique properties: a high refractive index (almost as high as in diamonds), hardness, refractoriness and resistance to chemical aggressors. All these properties, coupled with the fact that they are relatively inexpensive, explain their success in science and technology where they are used as material for lenses and prisms, "windows" in apparatus concerned with high temperatures and chemical aggressors. Fianites also make a fine laser material.

Nevertheless, it will probably be correct to say that the atomic power industry, today consuming more than 90 per cent of all hafnium produced, will retain its monopoly use of this metal for years to come. This is only natural, considering that this industry is one of the most important areas of modern technology.

Re

THE SECRET OF OLD WASTE DUMPS (RHENIUM)

A good offer.— Vacancies in the elements table.— False pretenders.— In search of the elusive elements.— A doubt is cast.— Apartment remains untenanted.— The last of the Mohicans.— The river that lent its name to an element.— On the top of a pyramid.— Going deep underground.— How much is a pound of rhenium?— An incredible octet.— Along the boundaries.— Wonderful filaments.— Contacts should be safe.— Aided by computers.— A new protective coating.— Splendid catalyst.— Distinguished guests.

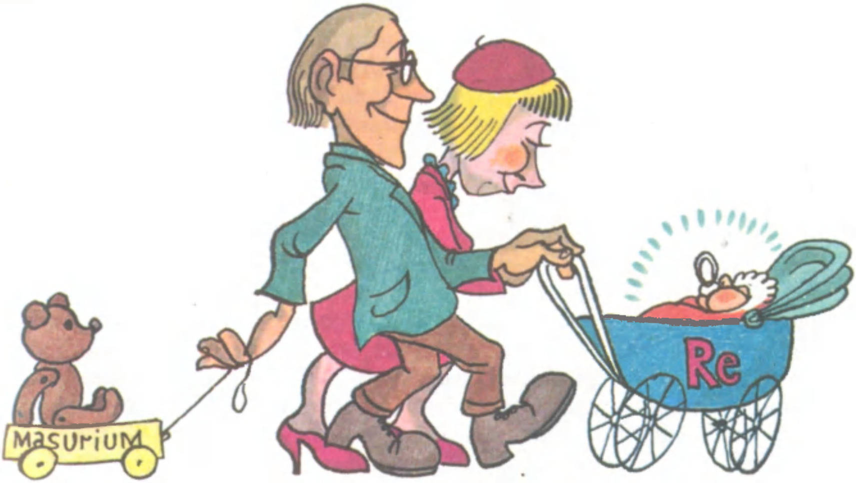
At the end of the 1920s a large foreign firm made what seemed a good offer to the director of a non-ferrous metals plant in Siberia: it wanted to buy the waste dumps on the plant premises for a handsome sum of money.

The officials rightly guessed that it was not the welfare of a Soviet enterprise that the firm had in mind but some special reason of its own. The staff chemists were instructed to analyze the old dumps and very soon it became clear what the foreign firm was after: the wastes contained an extremely rare element, rhenium, discovered a few years previously. Since the world production of rhenium was then measured in grams, the price of it was really fantastic. Small wonder that the firm's representatives were ready to pay a lot for the wastes. But they were refused, naturally.

What is rhenium and why such a keen interest in it?

The metal was discovered by Ida and Walter Noddack, but there were quite a few people before them who thought the credit belonged to them. As early as 1871 Mendeleyev predicted that there had to exist two chemical analogues of manganese in nature and that they were to be situated in the periodic table beneath this element, taking up squares Nos. 43 and 75. Mendeleyev called them, arbitrarily, eka-manganese and dvi-manganese.

Immediately there were more than enough pretenders to the vacancies. The history of chemistry abounds in mentions of new elements that were "opened up" only to be "closed down" upon careful examination. The same happened to the analogues of manganese. Many chemists in many countries claimed the discovery of these mysterious elements (e. g. ilmenium, davium, lucium, nipponium) but they were all at fault. But we must not be as categoric in the case of davium. Discovered in 1877 by the Russian chemist S. Kern and named in honour of



Sir Davy, the famous British chemist, davium became known for a specific chemical reaction which in our day is used to detect rhenium. We could suppose, perhaps, that Kern might have indeed come across grains of the dark, silvery metal which was officially born as rhenium fifty years later. At any rate, in Kern's day squares Nos. 43 and 75 remained "untenanted."

The period of uncertainty about the analogues of manganese lasted until the quest for the missing elements was joined by Ida and Walter Noddack. In 1922 they started a series of experiments with platinum ore but were soon compelled to turn to a "simpler" material, as they were running into quite an expense. Furthermore, their theoretical research into the question had by that time convinced them that elements Nos. 43 and 75 had to be concealed in minerals of the columbite type. They also managed to determine the approximate content of those elements in the earth's crust: to each of their atoms there were thousands of millions of atoms of other elements. Now it became perfectly clear why the "apartments" 43 and 75 had stayed vacant for such a long time.

The Noddacks' experiments were striking in the amount of effort that went into them: making use of X-ray spectroscopy, a method developed not long before, the scientists examined, within one year, 1 600 minerals occurring on earth and 60 meteorites. Their work was crowned with success: in 1925 they announced the discovery of elements No. 43 (masurium) and No. 75 (rhenium) in columbite.

But to announce the discovery was not all. It was necessary to prove it to those that would call it into question. One of the scientists who doubted that the time had finally come to close the vacancies in the elements table was the German chemist Prandtl. An important theoretician and brilliant experimenter, Prandtl became involved in a heated debate with the Noddacks. But they were prepared to defend their reputation at any cost. Finally, the duel between the two parties, which was followed by the scientific world with great interest, ended in a draw: the Noddacks had failed to furnish convincing proof of the discovery of masurium, but as far as rhenium was concerned, by that time its existence had been proved conclusively enough: two milligrams of the metal were isolated in 1926 and a year later, 120 milligrams.

The works of other scientists — F. Loring of Britain and the Czechs I. Druze, J. Geyrowski and V. Doleijek (they discovered rhenium in manganese ores independenty of the Noddacks several months later) — confirmed that the true owner of one of the vacant "apartments" had indeed been found.

Rhenium was really "the last of the Mohicans", that is, the last of the elements discovered in natural minerals. Subsequently a few more squares in the periodic table were filled, but those were elements obtained artificially, by means of nuclear reactions. The first among them was masurium, or element No. 43, named by its discoverers, the Italians Segre and Perrier, technetium.

The name rhenium is derived from the river Rhine, the homeland of Ida Noddack (it will be noted that not a single other element owes its name to a river). The commercial production of rhenium developed in the early 1930s in Germany where molybdenum ores containing as much as 100 grams of rhenium per ton of the ore had been discovered. A drop in the ocean, you might think, but in the case of rhenium this is considered an uncommonly high concentration, for the content of this element in the earth's crust is tens of thousands of times lower. Few elements occur in smaller quantities than rhenium.

If we arrange the chemical elements in a pyramid, with the most widespread ones (oxygen, silicon, aluminium, iron and calcium) forming its base and the rest situated on levels above, in accordance with their distribution in nature, rhenium will form its very tip.

Academician Fersmann belived that rhenium had an "affinity" to the zones of the globe that are situated the closest to its nucleus. It is possible that when future geologists succeed in reaching the very depths of the planet they will discover a great deposit of rhenium there.

In 1930 the world production of rhenium was ... three grams, and each gram cost 40 000 marks. Ten years later, however, Germany alone turned out approximately 200 kilograms of this metal.

Since then the interest in rhenium has been growing in all countries which can probably be explained by its unique properties. It is one of the heaviest metals, almost three times as heavy as iron. In density it is only slightly inferior to osmium, iridium and platinum. Its refractoriness (melting point 3 180°C) is extraordinary and second only to tungsten. As to its boiling point, it is so high that it has yet been impossible to determine it accurately, and can only be said to be close to 6 000° C (only tungsten's boiling point is close to this value). Furthermore, it is characterized by high electrical resistance.

Rhenium is a striking element in its chemical properties as well. Not a single other element can form eight oxides. The valency in this "octet" varies from 1 to 8. Rhenium is also the only metal that can form negatively charged univalent ions.

Rhenium is very stable in the air and when exposed retains its lustre for dozens of years. In this respect it is comparable to gold, platinum and other noble metals. Its corrosion-resistance is extremely high. Of all the most aggressive acids — fluoric, hydrochloric, sulphuric and nitric — it is affected only by the last one.

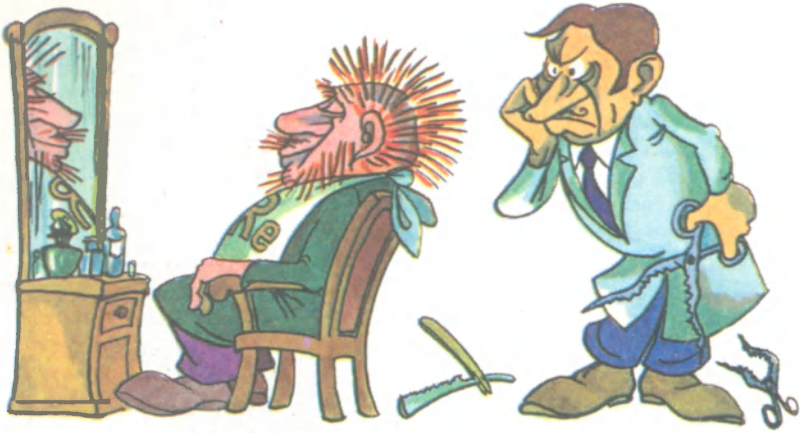
The valuable properties of rhenium explain its diverse applications in industry, the most important being its part in developing acid-resistant and refractory alloys. Twentieth-century technology is making tough demands on structural materials. In some cases it takes years to create an alloy answering certain specifications.

However, there is every reason to say that owing to rhenium scientists have made considerable headway in this sphere. Designers, especially, have a high regard for the refractory alloys of rhenium with tungsten and tantalum, which retain their valuable mechanical characteristics at temperatures as high as 3 000°C.

Of special interest to metal researchers is the so-called rhenium effect, that is, the beneficial influence of rhenium on tungsten and molybdenum, which, while having a high melting point and being capable of standing considerable loads, are very brittle under ordinary conditions (not to mention even a mild frost) and on impact may break like glass. But alloyed with rhenium they make hard alloys retaining their ductility even at low temperatures.

The nature of rhenium effect is not yet quite clear. Scientists believe that it may be attributed to the difference in the way these metals react with hydrogen. It is a fact that in the course of the production process tungsten and molybdenum may sometimes become "infected" with hydrogen. Since these metals do not dissolve hydrogen, it forms very thin carbide films along the grain boundaries, owing to which they become brittle. But rhenium added to tungsten or molybdenum makes the metal ductile by removing hydrogen from the boundaries and transforming it into a solid solution where it is practically harmless. This is why foil or wire made from alloys of tungsten with molybdenum and rhenium can be several times thinner than the human hair.

It has been found that rhenium alloyed with molybdenum is the best material for torsions, the extremely thin (several dozens of a micron) but incredibly strong filaments essential to super-precision



navigational instruments. The strength of this alloy (50 per cent of rhenium) is such that a wire one millimeter in diameter made from it can hold a load of hundreds of kilograms.

We come across electric appliances and instruments wherever we turn in our age of technology. All of them are equipped with countless switches, contacts, fuses, etc., and the development of appropriate materials for them has always been one of the most important areas of research.

The tiny spark we sometimes observe when turning on a switch should not be dismissed as harmless: sooner or later it will destroy a contact and lead to a loss of electricity. If we think in terms of countless contacts, it will only be too easy to imagine the inevitable power drain. The strength of contacts is especially important in cases when they work under a high temperature or in a humid atmosphere — factors greatly enhancing the danger of a breakdown. Scientists have never stopped their search for super-refractory and strong materials for the contacts. Tungsten was considered one of the best such materials for a long time. When the special properties of rhenium were discovered, it became clear that this metal was even better than tungsten. For instance, tungsten contacts could remain operative under vibration or in tropical conditions for only a few days before breaking down completely. Rhenium contacts work under the same conditions for months or even years.

But is it possible to produce enough rhenium to satisfy electrical engineering? Experience shows that contacts should not necessarily be made from pure rhenium. Almost the same effect is achieved by adding a little of it to tungsten. And it is not too costly: one kilogram of rhenium is enough to make tens of thousands of contacts.

One of the alloys of tungsten with rhenium produced in the Soviet Union is being applied in more than 50 vacuum electronic devices. Used for the cathode assemblies in cathode-ray tubes, this metal increases their service life to 16 000 hours. This means that a TV set working on such tubes for four hours a day will last at least 12 years.

Alloys of rhenium with niobium, nickel, chromium and palladium are characterized by remarkable properties: a small addition of rhenium to a chromium-nickel alloy raises its melting point by something like 200-250 degrees.

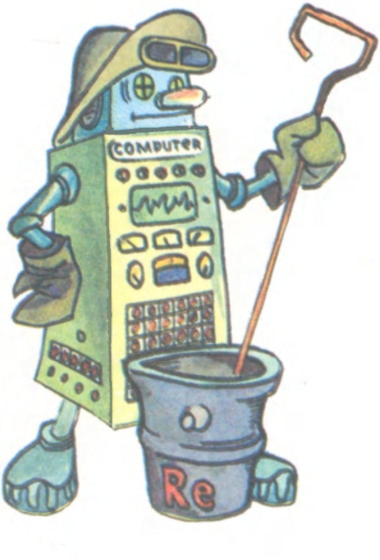
The range of applications of rhenium is vast — from extremely sensitive thermocouples successfully resisting the action of molten steel, to fountain-pen nibs, and instrument components of which great wear resistance is required.

The number of alloys of rhenium with other metals is constantly growing. In this field scientists today make wide use of computers. In the case of rhenium, computers have already predicted many valuable binary alloys.

Many ways to combat corrosion, and among them, chromium-, nickel- and zinc-plating, have been practised for years. One of the comparatively recent developments is rhenium-plating which is incomparably more efficient in protecting metals from the action of acids, alkalis, sea water, sulphurous compounds and other substances. Tanks made from rhenium-plated steel sheets are used for the transportation of hydrochloric acid.

Rhenium-plating increases the life of tungsten filaments in incandescent lamps and electron tubes several times over. It is impossible to remove all traces of oxygen and water vapour from the bulb during evacuation, and the same is true of gas-filled bulbs. If tungsten filaments are coated with rhenium, oxygen and vapour can have no harmful effect. As to the expense involved, it is really not big: one gram of rhenium is enough to make hundreds of metres of rhenium-coated tungsten filament.

Very important and rather new is the use of rhenium as a catalyst. It has been established that metallic rhenium and many of its alloys and compounds (oxides, sulphides and perrhenates) make fine catalysts for the oxidation of ammonia and methane, the production of ethane from ethylene and of aldehydes and ketones from alcohol, as well as for oil cracking. Rhenium powder capable of absorbing large volumes of hydrogen and other gases is the most promising catalyst. Specialists estimate that half of the world production of rhenium will be used for "catalytic" purposes within the next few years.



Thus, it is clear that rhenium cannot be threatened with "unemployment". But its great scarcity and dispersed state in nature are formidable obstacles in the way of its large-scale application. The earth's crust contains five times more gold than rhenium, 100 times more silver, 1 000 times more tungsten, almost a million times more manganese and 50 million times more iron. No rhenium deposits have been discovered and there is practically only one mineral — jezkazganite (found near the city of Jezkazgan in Kazakhstan) — that can be regarded as a rhenium mineral. As a rule, it is admixed with molybdenite (up to 1.88 per cent), columbite, pyrite and some other minerals, containing not more than milligrams or a few grams of rhenium per ton. Small wonder therefore, that the Noddacks had to process more than 600 kilograms of Norwegian molybdenite to obtain one gram of relatively pure rhenium. Specialists maintain that the reserves of rhenium in all the mineral deposits in capitalist countries come to only 1 000 tons.

Understandably, rhenium is much more expensive than gold and yet the demand for it has been growing, especially during the last few years when it has attracted the attention of spacecraft designers.

Until recently, rhenium in the Soviet Union was extracted from copper and molybdenum ores. At the end of the 1970s workers at the Institute of Metallurgy and Ore Dressing of the Kazakh Academy of Sciences developed a process of obtaining this metal from the semi-product of lead. It is based on ion-exchange processes yielding high-purity metal.

In 1960 a significant event took place at the Baikov Institute of Metallurgy of the USSR Academy of Sciences: it was visited by Ida and Walter Noddack. In itself, the fact that foreign guests should pay a visit to an institute of world renown was nothing out of the ordinary, but a visit by the Noddacks, the discoverers of rhenium, was certainly a special occasion. And it was no mere curiosity that brought the scientists there: the staff of the laboratory of rare-earth and high-melting metals under Ye. M. Savitsky, corresponding member of the USSR Academy of Sciences, had been engaged in a special study of rhenium for several years by then and had obtained very important results, promising this metal a brilliant future.

Os

AN INSULT TO A NOBLE METAL (OSMIUM)

Trifili or Varakhassi?— Wounded feelings.— A search is on.— Chlorine and rotting radish.— A noble origin.— Three champions.— Each in its right place.— Doubtful advantage.— What is the price?— Admirable hardness.— The secret of perpetuity.— The inseparable two.— A responsible job.— Worth the trouble.— In great demand.— Seven brothers.— Exclusive goods.— Poison!— In a glass of water.— Time to clear up the confusion.— Difficulties of employment.— The metal is trapped.

We begin our story about osmium by quoting a passage from *The Overcoat*, one of the best stories by the Russian classic writer, Gogol: "Akaki Akakiyevich was born, if my memory serves me right, on the night of 23rd March... The mother was presented with the choice of three names, namely, Mokkiy, Sossiy, or, it was suggested, the child might be called after the martyr Khozdazat. 'Oh dear,' thought his late mother, 'they're all such queer names'. To please her the calendar was opened at another place, but again the three names that were found were rather uncommon, namely, Trifili, Dula and Varakhassi. 'Bother,' said the poor woman, 'what queer names. I've really never heard such names. Now if it had only been even Varadat or Varukh, but no, it would have to be Trifili and Varakhassi'. Another page was turned and the names in the calendar were Pavsikaki and Vakhtissi. 'Well,' said the mother, 'I can see that such is the poor innocent infant's fate. If that is so, let him rather be called after his father. His father was Akaki, so let the son be Akaki, too.' "

There is no way of telling if the British chemist Smithson Tennant spent as much time thinking of a name for osmium, one of the two chemical elements he discovered in 1804, but it seems obvious that osmium was as unlucky as the hero of Gogol's story: The Greek word from which the name osmium comes means strong smell, and the Russian name Akaki also suggests a word that has rather a "smelly" connotation.

You will agree that such a name can do no honour to a noble metal (and osmium is a noble metal representing the platinum group). The insult is even more stinging considered in the context of the beautiful names osmium's closest relatives have: palladium — in honour of Pallas Athena; iridium — from the Greek for rainbow; rhodium — a rose; and ruthenium — the Latin name of Russia.

Before going into the reasons why Tennant was so harsh on his "godson", let us recall some events that preceded the discovery of osmium.

In 1804 the well-known British chemist William Wollaston, having just decided to stop mystifying the scientific world (for details see the chapter on palladium) reported to a sitting of the Royal Society that he had discovered hitherto unknown metals, palladium and rhodium, in crude platinum. Both were contained in the part of platinum that dissolved in aqua regia and formed an insoluble precipitate which attracted many chemists like a magnet, as they justly suspected that it could contain some unknown element.

The closest to the truth were the French chemists Descotels, Fourcroy and Vauquelin. They noticed that when crude platinum dissolved in aqua regia it released black smoke, while the insoluble residue formed soluble compounds when fused with potassium hydroxide. Fourcroy and Vauquelin suggested that the unknown element volatilized in part as black smoke and the residue put up all the resistance it could to the aggressor and would not dissolve in it. They even hurried to give it the name "pten" (from the Greek *pteron*, wing).

But the name was short-lived: very soon Tennant was able to break up pten, proving that it was a natural alloy of two components. He called one of them iridium for the bright colours of its salts and the other osmium, owing to the fact that when dissolved in acid or water, the product of fusion, or osmiridium (the name by which pten came to be known subsequently), with alkali, liberated osmium tetroxide which had an unpleasant strong smell resembling at once chlorine and rotting radish. It was later found that the metal itself could also have a similar smell, only a little less offensive. It happened when crushed osmium was left exposed and oxidized gradually, transforming into the "fragrant" tetroxide.

Osmium is a greyish-white metal which boasts a noble origin. If you glance at the periodic table, you will see the family of platinoids, keeping more or less to itself, in its right corner. It consists of two triads. The upper one includes light platinum metals: ruthenium, rhodium and palladium (everything is relative: any one of this triplet is 50 per cent heavier than iron). The second consists of heavy-weight champions: osmium, iridium and platinum. Curiously enough, scientists had for a long time believed that in conformity with their growing atomic weights the order of these three should be platinum — iridium — osmium. But when Mendeleyev was working on his periodic table he had to verify and sometimes correct the atomic weights of many elements. Since the amount of work involved was too vast to cope with alone, he recruited the help of other chemists. One of the scientists recommended to him was Yu. V. Lermontova, a relative of the great Russian poet Mikhail Lermontov. Mendeleyev asked her to verify the atomic weights of platinum, iridium and osmium, concerning which he had great doubts, believing that of the three elements osmium should have the smallest atomic weight and platinum the biggest. Lermontova, an extremely capable chemist, conducted a series of accurate experiments and confirmed Mendeleyev's view. Thus each of the three elements was put in its right place.

Osmium has a record-breaking density — 22.5 g/cm^3. To balance an osmium weight requires more than 40 weights made from lithium, osmium's antipode. An ordinary bottle filled with powdered osmium is heavier than a bucket of water.

For all its uniqueness, the density of osmium finds practically no application. Unlike a high melting point, hardness, strength and other valuable properties of metals, great density has no special advantage to the element it characterizes. It is the same with people: they admire those that are strong, fast and agile, but only look with doubt and curiosity at someone who has great bulk or height.

Nevertheless, osmium has certain "business" qualities that cannot but evoke respect. It is for good reason that it is the most expensive of the noble metals, although the least "noble" among them (you will remember that crushed osmium cannot resist oxidation even at room temperature, while its "relatives" are famous for their extraordinary chemical stability). And yet, in 1966, the price of platinum on the world market was 4.3 times as high as that of gold and iridium cost 5.3 times as much as gold, while osmium cost 7.5 times as much as gold. Nature is to blame for this situation in large measure: not only has it failed to create osmium reserves, but managed to hide traces of this element so well (the content in the earth's crust is $5 \cdot 10^{-6}$) that isolating them is an extremely costly enterprise. While the world production of most metals is measured in thousands or even millions of tons, osmium is produced in kilograms.

One of osmium's good points is its hardness. Few metals can vie with it in this characteristic, which is why osmium is included in alloys characterized by the highest wear-resistance. Gold-nibbed pens are quite common. But gold is known as a rather soft metal and the pen has to cover, so to say, many kilometres on paper. Even though it is nothing like sandpaper, just a few metals can endure such a stress. It is only because nib-tips are made from alloys of osmium with other platinoids, most often, osmi-

ridium, that they can do their work. It will be no exaggeration to say that a nib "armoured" with osmium is perpetual.

Exceptional hardness, great corrosion- and wear-resistance and the absence of magnetism make osmiridium an excellent material for the tips of magnetic needles and for instrument and clockwork axes and pivots. Made from it are the cutting edges of surgical instruments and tools for decorative carvings on ivory.

In nature osmium and iridium form a very stable natural alloy and neither of them has been discovered in nuggets. But osmic iridium and iridic osmium are fairly well-known minerals (called respectively nevyanskite and sysertskite), with iridium prevalent in the first and osmium in the second.

Sometimes these minerals occur naturally, but more often form inclusions in natural platinum. The isolation of the components (refining) is an involved, multi-stage process at one point of which osmiridium is precipitated. To separate osmium from iridium is probably the most difficult and costly part of the work. But very often it is not even needed: the alloy finds extensive utilization in industry as it is and it is far less expensive than, say, pure osmium. (The isolation of the pure metal from this alloy requires so many chemical operations that merely to enumerate them will take up all the space available. The end product of the long technological chain is 99.9-per-cent pure osmium.)

Another good property of osmium, apart from hardness, is its refractoriness. Its melting point (about 3 000°C) puts osmium ahead of all its platinoid relatives and of most other metals. Owing to its refractoriness, osmium wrote a page in the biography of the electric lamp. In times when electricity still had to prove its advantages over heated gas as a light source, the German scientist K. Auer von Welsbach suggested that the carbon filament in the incandescent lamp should be replaced by an osmium one. After that the lamps became much more economical, while giving a pleasant, even light. But it was not for long that osmium held this important job: it was first replaced by the less scarce tantalum, and soon after, by tungsten, the most refractory of all the refractory metals and one which is still doing the work today.

A similar fate awaited osmium in its other field of application: the production of ammonia. The synthesis of this compound suggested by the well-known German chemist, Haber, in 1908 is inconceivable without catalysts. The first ones used in the process worked only under high temperatures (above 700°C), and besides, were not very efficient.

Attempts to find a replacement proved futile for a long time. The answer was found by scientists at the Higher Technical School in Karlssruhe (West Germany), who suggested a catalyst of finely grained osmium. (It must be noted that while being very hard, osmium is very brittle and can easily be crushed.) Experiments on an industrial scale showed that the method was worthwhile: the temperature of the process was lowered by more than 100°C and the output of ammonia went up considerably.

Despite the fact that subsequently osmium was ousted from this sphere as well (at present inexpensive but effective iron catalysts are used), it can well be considered that this metal marked a turning point in the solution of the problem of ammonia production. Osmium is still used as a catalyst today, particularly in hydrogenation of organic substances where excellent results are obtained. This is what explains the great demand for this metal on the part of chemists. Remarkably, chemistry uses up almost a half of world osmium production.

Osmium is a fascinating object for scientific research. Natural osmium consists of seven stable isotopes with mass numbers 184, 186 through 190 and 192. It is a curious fact that the smaller the mass number of an isotope, the less often it is found in nature. While the share of the heaviest isotope (osmium-192) comes to 41 per cent of all the osmium found, the lightest of the "seven brothers" (osmium-184) comes to only 0.018 per cent. Since the isotopes differ only in their atomic mass, it is extremely difficult to separate them. This is why the price of even infinitesimal quantities of some isotopes is stunning: one kilogram of osmium-187, for example, costs 14 000 000 dollars on the world market. True, scientists have lately learned to separate the isotopes by a laser beam and there is hope that the price of these "exclusive" goods will soon be reduced considerably.

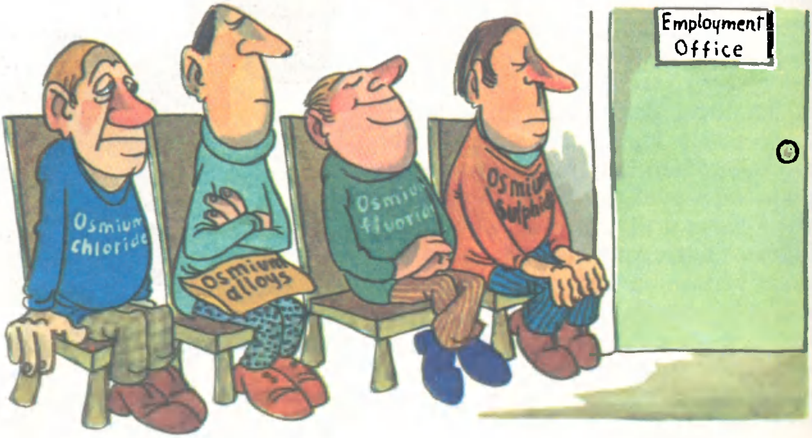
Just like other platinum metals, osmium can have different valency. More often it occurs in compounds where its valency is four or six but when it combines with oxygen, it usually "makes use" of all eight of its valency bonds. Of the osmium compounds, its tetroxide (the substance to which it owes its name) is the more commercially important one. It plays the role of catalyst in the synthesis of some drugs. It is also used as a pigment during microscopic examinations of animal and plant tissues. It must be borne in mind, however, that the pale-yellow crystals of osmium tetroxide are a strong poison affecting the skin, the mucous membrane and the eyes.

A peculiar property of osmium tetroxide is that its solubility in organic liquids is much greater than in water. Under ordinary conditions only 14 grams of this substance can be dissolved in a glass of water, but a glass of carbon tetrachloride will dissolve 700 grams.

Osmium powder flares up like a match in an atmosphere of sulphuric vapour and forms a sulphide. The omnivorous fluorine has no action on osmium at room temperature, but at 250-300°C a number of fluorides are formed. Since the first two volatile fluorides of osmium were obtained in 1913 the general belief was that their chemical formulas were OsF_6 and OsF_8. But in 1958 it was discovered that the fluoride OsF_8 of the chemical literature had never existed and that in real fact the fluorides were OsF_5 and OsF_6. Recently another fluoride — fluoride OsF_7 — was produced, which, when heated to above 100°C, disintegrated into OsF_6 and elementary fluorine.

The oxide of osmium is a black pigment used for patterns on chinaware, while its salts are powerful etching agents applied in mineralogy. However, most of osmium compounds, including its various complexes (osmium, like other platinum metals, is very good at forming complex compounds), as well as its alloys (with the exception of osmiridium described above, and some alloys with other platinoids, tungsten and cobalt) are still waiting for suitable jobs. But it can be stated for sure that the problem of their "employment" will soon be solved and they will reveal their hidden talents.

Meanwhile engineers and researchers are seeking economically effective ways of increasing the production of this valuable metal, and trying to find new sources of its extraction. Important results have been obtained at the Zavenyagin integrated non-ferrous works in Norilsk (extreme north of the Soviet Union). Metallurgists there had long been aware that the copper-nickel ores being shipped to the works contained metals of the platinum group, osmium included. But since its amount in the ore was minute it was ignored and the main attention was paid to turning out as much nickel and copper as possible.



Several years ago employees of the research centre of the Norilsk works attempted to extract osmium from the ore along with copper and nickel. The task was extremely difficult. It was necessary to find out what happened to osmium at the various stages of the working of the ore, to detect areas of its greatest concentration and determine the stage at which it was lost to waste. For that it was necessary to carry out numerous sophisticated experiments at every stage of the production process.

When that problem was solved it was necessary to develop a technique of capturing osmium from the furnace top gas and to design and build a proper industrial installation. The scientists and engineers at the Norilsk works overcame all the difficulties involved and osmium concentrate complemented the assortment of goods produced.

From Norilsk the osmium concentrate is shipped to the "mainland" where pure osmium, one of the scarcest metals, is isolated.

Ir

ALL THE COLOURS OF THE RAINBOW (IRIDIUM)

Following the storm of the Bastille.— Intolerable situation.— A time test.— Work record.— Helping out the heart.— A noble origin.— Cannot be afforded.— A coat of iridium.— Iridescent salts.— Some left-overs from the mint.— When tasting is dangerous.— The Minister's sanction.— In honour of Russia.— Bad news.—"I've suffered enough from it."— Warm congratulations.— Iridium comes last.— What is happening inside the bridge.— Looking into the blast furnace.— Thirteenth but lucky.— Iridium goes down into history.

On July 14, 1789, the insurgent people of Paris took the Bastille by storm, setting in train the French Revolution. Along with the decrees and resolutions of a political, social and economic nature, the revolutionary government passed a decision on the introduction of a metric system of weights and measures. A committee of the French Academy recommended the metre as the unit of lenght equal to one ten-millionth part of a quadrant of the Paris meridian. The recommendation was preceded by extensive geodetic surveys of the Barcelona-Dunkirk arc which had been conducted during a period of five years under the supervision of J. B. Delambre and P. F. Mechain, both prominent French astronomers and geodesists.

In 1797 the work was completed and two years later the first metre standard was manufactured. It was a platinum bar which came to be known as the "archival metre" as it was placed in special custody. The mass of one cubic decimetre of water drawn from the river Seine at 4°C was accepted as the unit of weight equal to one kilogram. The kilogram standard was made from platinum in the shape of a cylindrical weight.

As the years passed, it became obvious that the natural prototypes of these units — the Paris meridian and the water from the Seine — were not very convenient for reproduction and besides, were not at all constant values. That situation could not be tolerated by scientists for long.

In 1872 the International Committee on Weights and Measures abandoned the natural prototype of the unit of length and 31 metre standards were manufactured on the basis of the "archival metre". Those were also bars but the material used was not pure platinum but an alloy of this metal with iridium (10 per cent). Seventeen years later the same lot befell the water from the Seine: a weight made from the same platinum-iridium alloy was installed as the prototype of the kilogram and its 40 accurate replicas became the international kilogram standards.

There were good reasons why iridium was picked as a component in the alloy from which the standards were made. Being exceptionally strong and hard, refractory, wear- and corrosion-resistant and utterly indifferent to temperature changes in the atmosphere where it is kept it met all the specifications a material used for such purposes must meet. Pure platinum is not quite up to mark, but its alloy with iridium has coped with the difficult task for a century now. True, the "archival metre" has been forced to "resign" (in 1960 it was accepted as equal to a band of 1 650 763.73 wavelengths of orange light emitted by the isotope krypton-86) but the world's main kilogram is still valid.

The metrological services, however, are not the only occupation of platinum-iridium alloys. They go into the manufacture of refractory crucibles that easily survive great heating in aggressive media (such crucibles, among other things, are used for growing crystals intended for laser equipment). They are also a favourite with jewellers. An incomplete work record of these alloys includes parts of chemical apparatus, high-precision instruments, electric contacts, surgical instruments, springs and laboratory and other equipment.

Several years ago platinum-iridium alloys were introduced in cell terminals of electric pacemakers implanted in a heart patient. The electrodes of the pacemaker are inserted in the patient's heart and are connected to a tiny receiver (also in the patient's body) and a generator with a ring aerial fixed on the patient's body in the vicinity of the receiver or worn in a coat pocket. The moment there are signs of heart trouble the patient switches on the generator. The impulses it sends to the ring aerial are transmitted to the receiver, from there to the electrodes and, through the platinum-iridium terminals, to the nerves stimulating the heart's activity.

Alloys of iridium with other metals are characterized by many valuable properties as well. Widely used is osmiridium, the natural alloy of osmium and iridium (for greater detail see the chapter on osmium). Small additions of iridium to tungsten and molybdenum enable them to retain their strength characteristics at high temperatures. High as the acid resistance of titanium and chromium is, an addition of iridium to these metals makes them exceptional in this respect.

The reader must not get an impression, however, that it is only in alloys that iridium finds application: it is as useful in its pure state. Apart from the fact that this silvery-white metal looks beautiful, it also has excellent physical characteristics. It is hard and strong and shows good resistance to high temperatures, wear and other dangers. Its striking feature is great density (22.4 g/cm^3), in which respect it is only inferior to its closest neighbour, osmium. Along with the other members of the platinum group, it belongs to noble metals, hence, is not affected by any acids either under ordinary or high temperatures. Even aqua regia, one of the worst aggressors known, is powerless to produce even

the slightest effect on it. The only substances affecting it are molten alkalis and sodium peroxide.

One of iridium's greatest advantages is an ability to retain its valuable properties practically indefinitely whatever the changes in the medium. But for its high cost (it is more expensive than platinum), it would have been used in many fields of science and technology. But as it is, its application is limited to where it is practically irreplaceable. For instance, it is the material from which laboratory crucibles are made, intended for experiments with the forbidding fluorine and its aggressive compounds. The orifices of blowpipes used in the manufacture of refractory glass are also made from iridium. Along with its alloys with ruthenium or rhodium, iridium is introducted in thermocouples measuring high temperatures (2 000-2 300°C). So far such thermocouples have been used only for research purposes which is due to their high cost.

Very promising are the extremely strong iridium coatings. That these coatings are not in use on as large a scale as, say, platinum, palladium or rhodium coatings, is perhaps to be explained by the technical difficulties the process of deposition of iridium on other metals involves. Iridium coatings can be deposited electrolytically from the molten cyanides of potassium and sodium at 600°C. The other process — cladding — is much simpler. This is achieved by applying a thin layer of iridium to some other metal and placing it under a hot press which causes the coating to stick tightly to the base metal. The same process is used for the manufacture of iridium wire: a bar of tungsten or molybdenum is introduced into an iridium tube and by means of hot forging and drawing a bimetal wire of necessary thickness is manufactured. It is used for the control grids of electron tubes.

There is also a chemical process of iridium-coating. It consists in depositing a solution of an iridium salt with phenol or some other organic compound on the surface of an article, and heating it in a controlled atmosphere of up to 350-400°C, during which the organic substance volatilizes and a layer of iridium is left on the surface of the article.

Alloyed with other metals or in pure form, iridium is applied in the chemical industry: iridium-nickel catalysts take part in the production of propylene from acetylene and methane; platinum catalysts, also containing some iridium, accelerate the formation of nitric oxides — one of the stages in the production of nitric acid.

Extremely beautiful are the bright-coloured iridium salts, although except giving this element its name, this quality has found no practical application so far. It will be recalled that in 1804 Smithson Tennant discovered two new elements in the black residue of native platinum dissolved in aqua regia. Since one of them formed salts of all the colours of the rainbow, Tennant did not have to spend much time thinking of a name for it. He called it iridium from the Greek *irioeides* — iridescent.

The fates of the platinum metals are so intimately intertwined that it is impossible to tell about one of them without digressing into the histories of the others. In 1840 Professor of Kazan University (Russia) Karl Klaus, we have mentioned earlier, became interested in processing platinum ore found in the Urals. At his request the St. Petersburg Mint sent him samples of platinum residues, that is, the insoluble precipitate formed when crude platinum is processed by aqua regia. Subsequently he recalled: "At the very beginning of my work I was struck by the amount of valuable components my residues contained: apart from 10 per cent of platinum, I extracted a considerable amount of iridium, rhodium, osmium, a quantity of palladium and a peculiar mixture of metals..."

While initially Klaus had only a purely practical end in mind — to find a way of processing the residues of platinum ore into platinum, he was soon completely absorbed in more fundamental research. "For two full years", he recalled, "had I been busy with this problem from morning till night. I lived in the laboratory, I dined and had tea there and became an awful empiricist into the bargain." The last remark had a perfectly concrete meaning: according to the outstanding Russian chemist Alexander Butlerov, Klaus' pupil, his teacher "was in the habit of stirring platinum ores in aqua regia with all his five fingers and checked the concentration of the acids that had shown no reaction by tasting them." As a matter of fact many chemists of the old school tasted any substance obtained (up to the mid-19th century any description of a chemical substance had to mention also its taste) and ran grave risks.

Thus it happened that the famous Swedish chemist, Karl Scheele, died on tasting hydrocyanic acid.

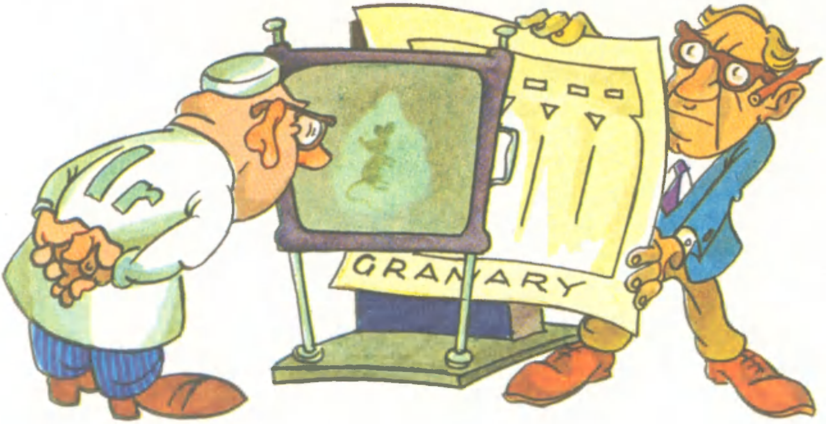
Klaus' work was crowned with success: he found a way of processing the residues. Now he had to go to St. Petersburg to report the results to the Minister of Finance who had been interested in the problem. To make the trip the chemist had to borrow 90 roubles from a friend (he was able to repay it not until several years afterwards when he was already known internationally). On arrival in Russia's capital Klaus was received by the minister two days later and given sanctions to be issued 0.5 pound of platinum residues and a quarter of a pound of crude platinum to continue his research.

Back in Kazan, Klaus plunged into his studies once more and a few years later could boast brilliant success. One of the most important results was the discovery, in 1844, of the last unknown element — the "Russian" member of the platinum family. Klaus wrote: "I noticed even during my first experiments that there was a new substance present, but was at first unable to isolate it from the admixtures. I worked on the problem for more than a year before I finally developed an easy and reliable way of producing it in its pure form. This new metal, which I called ruthenium in honour of our fatherland (from the Latin name for Russia — *Ed.*), doubtlessly belongs to substances of great interest."

However, Klaus' discovery was not immediately recognized. He sent the first samples of some compounds of the new element to Berzelius (in Stockholm) who commanded the greatest respect of all chemists. We can only imagine Klaus' disappointment when he learned that the celebrated scientist believed the substance sent to him contained not a new element but was an impure compound of iridium. Convinced that he was right, Klaus conducted experiment after experiment, at times ignoring even the most elementary precautions. A few years later Klaus warned his colleagues: "When working with osmic iridium one must beware of the vapours of osmic acid. This extremely volatile substance is among the most dangerous substances, which affects primarily the lungs and eyes, causing bad inflammations. I have suffered enough from it." Klaus' desire to convince the scientific world that he had really discovered a new element was so great that he finally achieved his end. Ruthenium compounds were once more dispatched to Berzelius who, upon careful examination, realized at last that he had made a mistake. "Please accept my sincere congratulations on your brilliant discoveries and their elegant presentation. Owing to them, your name will be inscribed in the history of chemistry for all time," he wrote to the Russian scientist.

Klaus summed up his work in a paper entitled "Chemical Study of Residues of the Urals Platinum Ore and the Metal Ruthenium" published in 1845, which also included the first-ever description of iridium in which Klaus noted that he had spent more time on iridium than on other platinum metals. His recommendations became the basis for developing the production of iridium and other platinoids. At present pure iridium is extracted from native osmiridium and the residues of platinum ores by acting on them by various reagents. First platinum, osmium, palladium and ruthenium are isolated and only then comes the turn of iridium. The powder thus obtained is either compacted and then melted, or is melted in electric furnaces in an atmosphere of argon. At ordinary temperatures iridium is extremely brittle and cannot be worked in any way, but when hot, it can be forged.

Iridium is very scarce: its natural reserves are not more than a few millionths of one per cent. The total yearly production by all countries is not more than one ton. However, this fact does not dampen scientists' interest in this element. Increasingly more fields of application are found for the radioactive isotopes of iridium. Not long ago researchers at the Quadarash atomic research centre in France designed a flaw-detector (gammatron) for the control of the state of bridges, dams and other reinforced concrete structures: under the action of gamma-rays emitted by the isotope iridium-192 a glass plate with a light-sensitive layer deposited on its surface shows a clear picture of the "insides" of the units and parts being inspected. By means of such flaw detectors the quality of hardware and welds is checked: the photofilm lays bare all cavities, spots of poor penetration and foreign inclusions. In blast furnace production small-sized containers of the same isotope control the level of the charge in the furnace. Since fractions of gamma-rays are absorbed by the charge, it can be determined accurately enough what dis-



tance the rays cover travelling through the charge, that is, to determine its level.

A few more words on the isotopes of iridium. Apart from the iridium-192, we have mentioned, there are 14 other radioactive isotopes with the mass numbers from 182 through 198. The heaviest of them has the shortest life: its half-life period is less than one minute. Curiously, in iridium-183 this period is exactly one hour. Only two isotopes — iridium-191 and iridium-193— are stable. The share of atoms of the heaviest of them in the natural isotopic mixture is something like 62 per cent.

Associated with an isotope of iridium was the discovery of Mössbauer effect which is the basis of extremely accurate methods of measuring minute quantities and weak phenomena, widely used in physics, chemistry, biology and geology.

To date Mossbauer effect has been confirmed by experiments with several dozen of elements, but the history of science will always associate the discovery of this important physical phenomenon with iridium.

Tl

BUDDING TWIG (THALLIUM)

He who seeks shall find.—"Eureka!"— A find in dust.— When new leaves come out.— Discovered a second time.— Spiritualism and chemistry.— In honour of Avicenna.— Laurels for the platypus.— The terror of rodents.— Seeing in darkness.— Precious stones?— Flashes in the crystals.— Good catalyst.— But for one circumstance.— Agatha Cristie makes a diagnosis.— Separating the inseparable.— Thallium in semiconductors.— The lights of a big city.— In company with other metals.— A valuable contribution.— Under freezing temperatures.— In the service of industry.— The lightest isotope. — In jellyfish and beet roots.— Thallium is yet to have its say.

"He who seeks shall find," goes a popular Soviet song. Whether this is true or not, one thing is definite: at all ages of history people have been looking for something, some for treasure, others for adventure and still others for a path into the unknown. At times they did find something. The great Archimedes found a brilliant solution to the problem of the gold-to-silver ratio in the crown of King Hieron of Syracuse when he was lying in a bathtub. Oblivious of his surroundings, Archimedes ran out into the street without a stitch of clothing on, shouting "Eureka!" (I've found it!), although passers-by must have been sure he had lost everything.

It happened sometimes that while seeking a treasure one found a few grains of lead, and with it, eternal peace. On the other hand, Columbus, who had failed to find a short cut to India, found a whole new continent. Something of this nature happened to Sir William Crookes of Britain in 1861 when he discovered thallium. But it all started much earlier.

Back in the 1850s Crookes, then a young chemist, was engaged in a study of flue-dust accumulating in the process of sulphuric acid production, believing it might contain tellurium. But his numerous chemical experiments did not yield any positive results and he lost all interest in the work. He left the dust abandoned for a long time in his laboratory until the discovery of spectral analysis brought it back into his mind. The new method was not as labourous as the chemical one and the scientist decided to try it out.

To his great surprise, instead of the line of tellurium Crookes observed a bright green line which was foreign to all then known

spectra. He realized he had discovered a new element, and since it was spring and new leaves were just coming out on the trees, he called it thallium (from the Greek *thallos*, budding twig).

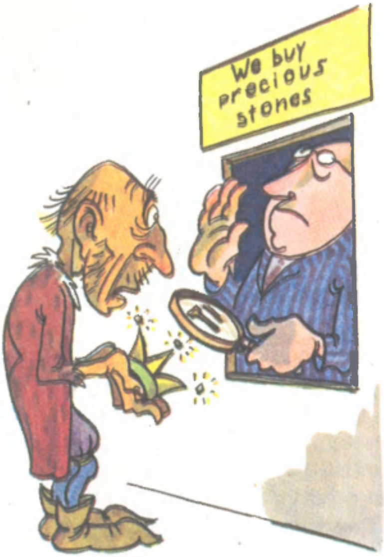
A few months later thallium was discovered by the French chemist, Lamy, also in flue-dust of sulphuric acid production and also spectroscopically. Even though Lamy was able to isolate 14 grams of metallic thallium and determine some of its properties, the priority of the discovery belongs to the British chemist. Subsequently William Crookes made a considerable contribution to the development of chemistry and physics and in his declining years headed the London Royal Society. (Paradoxically, with all that Crookes was a dedicated spiritualist and spent much time communicating with the spirits.)

The fact that thallium was for the first time detected during a spectroscopic examination was natural: this element is present in most minerals in such minute quantities that to discover its traces by chance chemically is practically impossible and it was only owing to the exceptional accuracy of the spectral method that it was discovered at all. The overall content of thallium in the earth's crust is not so small —0.000 3 per cent (the reserves of, say, gold or platinum are far less). On the other hand, there are only five types of rock that can be regarded as thallium minerals: lorandite, hutchinsonite, urbaite, crookesite and avicennite. The last of these, which is almost pure thallium oxide, was found in 1956 in Uzbekistan (the Soviet Union) and named in honour of the great physician and philosopher of antiquity, Avicenna (Abu Ibn Sina). These minerals occur so seldom in nature that there can be no question of their commercial exploitation as thallium ores. Generally, metallic thallium is obtained as a by-product during the production of lead, zinc and some other metals.

For more than 50 years after discovery thallium remained strictly an object of scientific research and as such was found to present striking peculiarities. In appearance, density, hardness, melting point and other physical characteristics it has much in common with lead, its neighbour on the right in the elements table (the two occupy squares Nos. 81 and 82). Chemically it has some common properties with sodium and potassium and also with silver.

Being a representative of the third group, thallium should mostly act as a trivalent element, but it "prefers" to be univalent like the alkalis. In some complex compounds, however, both univalent and trivalent thallium is present: the first in the role of the cation, the second as a component of the complex anion. This is how a well-known French chemist, Dumas, described element No. 81: "It will be no exaggeration to say that from the standpoint of accepted metals classification thallium combines opposite properties which makes it possible to call it the ornithorhynchus paradoxus of metals." To illustrate his point, Dumas said that among metals thallium was as much a paradox as the platypus among animals. (This strange creature is a mammal but like the amphibia and birds it lays eggs and is also striking in appearance: it is covered with fur but has a duck-bill and webbed feet.)

As more information about thallium and its compounds accumulated, some practical uses began to be found for it. For the first time it happened in 1920 when a rodent and insect killing poison containing thallium sulphate was patented in Germany. The same year it was noticed that the action of light on oxisulphide of thallium — thallophide — changed its electrical conductivity, and also that it was particularly sensitive to infrared rays. The result was that soon thallophide cells were developed and found application: in singal devices operating in darkness or thick fog, in infrared lights indicating landing sites for aircraft coming in at night, in devices spotting heated objects in darkness, in instruments gauging stellar radiation, in photographic exposure meters for photography in infrared rays. The use of other thallium compounds, such as the bromide and iodide of thallium, is also based on its extraordinary transparency to infrared rays. The single crystals of these salts are used in lenses, prisms and cells for optical instruments operating in the infrared region of the spectrum. Thallium salts are included in the composition of special-purpose glasses — yellow, green and orange of great refractive power (they can even serve as imitation gems) and also in the composition of black opaque glass.



Widely applied in modern engineering are scintillation counters, i. e., instruments for detecting and measuring radioactive radiations, whose principal components are phosphor crystals producing light flares when hit by beta- or gamma-radiation. By means of a photocell, light is transformed into electricity and, the more intensive the radiation, the brighter the flare and the greater the strength of the current. The halides of alkali metals play the role of phosphor crystals. Added to them are so-called activators which make the halides more efficient and create focuses of luminescence in the crystals. In the scintillation counters the phosphor activator is thallium.

In chemistry thallium and its oxides and sulphides are applied as catalysts in many organic reactions (e. g. hydrogen reduction of nitrobenzene, oxidation of gaseous aniline, etc.). Some thallium compounds can serve as antiknock additives to petrol.

But for one circumstance, thallium and its salts could have found extensive application in medicine. This circumstance is the high toxicity of both the metal and most of its compounds. Since in many cases the dose that could produce a therapeutic effect is close to dangerous, the use of thallium is limited almost wholly to the treatment of ringworm of the scalp (as a hair-removing agent) and to some other "small jobs".

A curious incident that happened several years ago was associated with thallium. A small girl, one and a half years old, in need of urgent medical help was flown by her parents from Qatar, a small Arab sheikdom in the Persian Gulf, to London. The patient was in a serious condition: her blood pressure was rising every day and it was increasingly hard for her to breathe. Doctors in Qatar had failed to diagnose the disease and London specialists were the girl's parents' only hope.

But when she was brought to a London hospital it appeared that even the most skilled doctors could not make anything of the strange disease, and after several hours of consultation, had reached no agreement on the case. Meanwhile the girl's condition had deteriorated and became grave: she was unconscious most of the time. Finally, when the situation seemed hopeless, a nurse who was attending to the patient came up with the suggestion that the girl was suffering from thallium poisoning. She explained that a novel by Agatha Christie she had read not long before had a description of thallium poisoning and that the symptoms given there bore a striking resemblance to those shown by their patient. The doctors decided to check the nurse's version but the hospital did not have the necessary instruments and reagents. Help arrived from... Scotland Yard, which, by a happy coincidence, had just dealt with a case of thallium poisoning. Its laboratory provided the necessary chemicals and instruments. The nurse's diagnosis proved correct: the girl was indeed suffering from thallium poisoning. It was later found that her parents had been using a rat poison based on thallium salts which had affected her. The patient was prescribed the necessary treatment and was soon out of danger.

Obviously, thallium and its compounds are not to be treated lightly, but if used properly, they can do good.

In nature most minerals are so well combined that it is sometimes extremely difficult to separate them. This is where some organic compounds of thallium come in handy. If such minerals are immersed in a water solution of thallium malonate and thallium formate (Clerici solution) a liquid characterized by high specific gravity (more than 4 g/cm^3), the lighter ones will come up to the surface and the heavier will form a residue. Apart from separating component minerals, this method also makes it possible to estimate their density.

Semiconductors, in fact a fairly recent invention, have become part and parcel of our life, not to mention technology to which they are indispensable. Semiconductor devices — simple, reliable and easy to handle — cope with an enormous amount of work. Among the many known substances with semiconductor properties, of special significance are so-called vitreous semiconductors which invariably contain thallium in various combinations with arsenic, antimony, sulphur, selenium and tellurium.

Along with other elements, thallium is employed in city electric signs flaring up at night: glass tubes filled with argon and thallium vapour produce a pleasant green light. Thallium vapour also gives a green light to some signal flares. Thallium discharge lamps are used for calibration of spectral instruments, for checking photographic films and negatives and for estimation of roentgenograms.

More than 10 000 alloys are applied in industry and agriculture, and it is hard to find a metal that is not a component of some alloy. Thallium has not been ignored here either. Readily fusing with other metals, it imparts to them certain valuable characteristics. Combined with lead, tin and antimony, it makes an excellent acid-resistant material for lining underground pipe-lines. Among recently developed alloys is a large group of bearing metals in which, depending on the purpose of the bearings, thallium is combined with different metals, including lead, copper, tin and sometimes even gold and silver. Owing to its rather low melting point, thallium in bearings forms a natural lubricant in the process of their operation, greatly improving their wear resistance.

There are several dozens of thallium-containing fusible alloys and the most striking of them is doubtlessly the amalgam of thallium

which solidifies only at minus 60° C. Thermometers filled with this liquid alloy are indispensable in the coldest parts of the world and in space, where common mercury thermometers are useless.

The radioactive isotope thallium-204 serves as a beta-radiation source in many instruments used to control production processes, and particularly, to gauge the thickness of moving textile or paper strip: the moment beta-rays passing through the layer of the material begin to lose or gain in intensity (which means that the material has gained or lost in thickness), an automatic device restores optimal operating conditions. Other instruments working on radioactive thallium remove harmful electrostatic charges that often originate in shops at textile and paper mills and factories manufacturing cine film.

Until recently scientists knew two stable and 18 radioactive isotopes of thallium. The isotope thallium-191 was considered to be the lightest of them. But in 1972 even a lighter one, thallium-189, was obtained at the Joint Nuclear Research Institute at Dubna near Moscow.

Traces of thallium are found in many plants and animals. Curiously, among animals the most conspicuous in this respect are marine species (actinias, jellyfish, starfish, etc.) and among plants, it occurs predominantly in species growing on the surface, some of which even accumulate it in the course of their life process. For example, thallium was found in beet roots growing in an area where the most sensitive instruments failed to register its presence. Subsequent research showed that sugar beet could "collect" and accumulate thallium even where it was present in soil in the minutest quantities.

More than a hundred years ago the French chemist Dumas we have mentioned earlier predicted that thallium would usher in a new epoch in the history of chemistry. He must have exaggerated the significance of the element to the study of which he had devoted all his life. On the other hand, it can be stated for sure that this element has not played its best roles yet.

Bi

A SPACE MISSION (BISMUTH)

Experiment *Sphere*.— Was it worthwhile?— Confusion in medieval chemistry.— Demogorgon or glaura?— Conjectures.— The pale faces of beauties.— A noble occupation.— The fire brigade may go to sleep.— Classroom tea party.— A plague cure.— Effect grows more effective.— In chinaware and cosmetics.— Stuffed polymers.— The best part.— Defying the laws of nature.— Between the poles.— Up in a blue flame.— A law is corrected. The molecules are realigned.— Metal glass.— Under fire for two months.— Almost scarce.— Finds beyond Lake Baikal.

On a summer day in 1976 Boris Volynov and Vitali Zholobov, the crew of the *Salyut-5* orbital research station, reported to the Flight Control Centre on the completion of a programmed technical experiment codenamed *Sphere*.

It is incredible just to think how many professions spacemen have to master. They are geologists, biologists, doctors, physicists and chemists — it is hard even to enumerate all their “celestial” occupations. This time, in order to carry out the experiment *Sphere*, they turned into metallurgists and their “shop” was a compact device by means of which they had to study the process of solidification of molten metal in weightlessness. To put it in more specific terms, they were to make use of zero-gravity in order to obtain ideally spherical metal balls.

What was the device and what was the metal destined to be among the first to go down in the history of space metallurgy? The device consisted of a box holding the metal pellets to be melted, an electric heater and a small transparent lavsan bag. The metal chosen by scientists was Wood’s alloy (bismuth, lead, tin and cadmium, in the ratio of 4:2:1:1 respectively) known to metallurgists for more than a hundred years. Its main advantage and the reason why it was sent on a “space mission” is a low melting point (around 70°C): the faster a metal melts the simpler, hence more compact, will be the device for melting it, and, obviously, there is no need to explain how vital this is in space engineering.

Precisely on the appointed hour the cosmonauts turned on the device and a tiny grain, resembling a piece of pencil lead, was charged into the tube of the heater. There it soon became a drop of molten metal and a special attachment pushed it into the lavsan bag. Were the experiment taking place on earth, the drop would have immediately fallen to the bottom and that would be it. In outer space though, on leaving the heater, the pellet of molten metal simply floats in weightlessness. The speed with which it is pushed out of the heater and the size of the bag are designed in such a way that by the time it touches the wall of the bag it should have solidified. So, drop after drop transformed into a tiny mat bead.

"The beads seem to look all right, they're nice," Vitali Zholobov commented as the experiment proceeded. "It's pleasant to watch the hot drops float in weightlessness and solidify without touching anything."

What was the point of the experiment? What was its practical use? Is it worthwhile to have a whole to-do in space for the sake of collecting a few beads, even if of an ideally spherical shape? But were they spherical?

The lavsan bag was brought to earth and scientists at many laboratories carefully studied the contents. Alas, it was found that in the process of solidification, instead of becoming round, the drops acquired an elliptical form and when cold, turned into tiny "pears" or "onions". Furthermore, Wood's alloy in space lost its uniformity. But since, as they say, "you must spoil before you spin well", we can suppose that such experiments will be continued. If they prove successful, alluring prospects will be revealed before technology: to make a ball for a bearing in terrestrial conditions it is necessary to carry out eleven operations and lose a substantial amount of metal. Besides, the structure of the surface layer of the ball does not always turn out ideal. It is to be hoped, therefore, that it will be possible to launch a ball-bearing plant in outer space one day and the expenses involved in the space journey of Wood's alloy will be repaid with interest.

But right now let us descend to earth and learn something about bismuth, the principal component of Wood's alloy. Bismuth is a silvery-white metal with a pinkish tinge. The first mention of it is found in the 15th century chemical literature, though in those days many chemists confused bismuth with lead, tin or antimony. In an alchemic dictionary, for instance, it is described as "any lightest, palest and cheapest lead". At the same time, in his book on mineral deposits and mines in old and new times, written in 1546, a well-known metallurgist and mineralogist, Georgius Agricola included bismuth among the most important metals known since ancient times: gold, silver, copper, iron, lead, tin and mercury. But still it was only in the 18th century that bismuth was finally defined as a distinct chemical element. It is probably correct to say that not a single other metal has ever had as many names as bismuth. According to some scientists, more than 20 names are found in the literature of the 15th-18th centuries, and among them such expressive ones, as demogorgon, glaura and nymph.

There are numerous versions explaining the origin of the word "bismuth". Some believe it is based on the German roots *wis* and *mat* (drived from which are *weisse masse* and *weisse materia* or white mass and white material) meaning white metal. Others think that it comes from the German *weise* (meadow) and *muten* (to work a mine), since even in old times the metal was mined in the meadows of Saxony near Meissen. Yet others assert that bismuth owes its name to Wiesen,

an area in Germany rich in this metal. There is also a theory that bismuth is a distorted version of the Arabic *bi ismid* which means looking like antimony. It is hard to say which version is authentic. The *Great Soviet Encyclopaedia*, for instance, does not give a definite answer and only remarks: "The origin of the name B. has not been established."

The symbol Bi was first introduced by the outstanding Swedish chemist, Berzelius.

In the old days bismuth compounds were widely used as pigments, grease-paints and cosmetics. In great demand among Russian women were all kinds of ceruse, including one based on bismuth which was also called Spanish ceruse. An Englishman, who visited Russia in the middle of the 16th century, commented that "women use so much paint that one can see their smeared faces almost at shooting distance. They can be best compared to millers' wives as they look as if flour bags were beaten out in front of them".

Medicine is another ancient "occupation" of bismuth compounds. To this day they are included in many drugs, powders and ointments used as an anticeptic and healing agent in the treatment of skin and gastrointestinal diseases, burns and wounds. The pharmaceutical industry, therefore, is one of the main consumers of bismuth.

In engineering bismuth has long been known for the fusible alloys it makes. In a book published more than a hundred years ago we read: "Bismuth is included in alloys for the sole purpose of making them fusible. This is why this metal is used by tinmen and organ-builders when they need an especially low-melting material. Printers also add a little bismuth to their metal so that it melts easier which, of course, does not improve its quality, as bismuth makes all alloys brittle."

Today printers have stopped using bismuth in type metal but there is plenty of work for bismuth alloys, and among them, Wood's alloy we have mentioned above, in other fields. For example, firemen have nothing to worry about if they know that inflammable objects and

buildings are equipped with automatic fire extinguishers working on fuses made from bismuth-based alloys. Once the temperature in a building rises above a definite value, the fuse melts, activating the relay which gives a sound signal. There are some devices that not only sound the alarm but flood the fire with water without any outside assistance, and when the firemen arrive the only thing they have to do is to return the device back to its state of "combat readiness".

An alloy of bismuth with lead and mercury melts even on rubbing and serves as a metal pencil. Bismuth-based fusible alloys make reliable glass-to-metal seals. A tea-spoon made from Wood's alloy will melt the minute it is put into the teacup. You will not find a spoon like that in a store, but at a physics lesson it impressively demonstrates the alloy's qualities.

Being a fine casting material, bismuth is used for the moulding of most intricate shapes, for filling section metallographic specimens and also in dentistry.

Certain bismuth alloys are characterized by unique magnetic properties. An alloy of bismuth with manganese makes powerful permanent magnets; an alloy with antimony, exhibiting the effect of magnetoresistance, is used for the manufacture of fast-responding circuit-breakers and amplifiers. Aluminium- and iron-based alloys with an addition of bismuth (a mere 0.01 per cent) demonstrate improved plasticity and workability. The same effect is achieved by adding bismuth to stainless steel. Combined with tin, bismuth prevents the latter from contracting what is called "tin plague", i. e. disintegration of the metal into powder under low temperatures. This is caused by the transformation of one modification of tin into another, whose crystalline lattice has a more widely spaced distribution of atoms (white tin is transformed into grey tin). The lattice is cemented, as it were, by atoms of bismuth which prevent it from destruction when its atoms are realigned in the process of transformation.

Alloys of bismuth with tellurium are considered a promising material for thermoelectrogenerators. In them, a good combination of the metals ensures high efficiency of transformation of thermal into electric power. It will be recalled that the first thermoelectric battery designed something like a hundred and fifty years ago worked on soldered antimony and bismuth wires.

Thermoelectric cooling is today widely used in cosmonautics, medicine and other fields. Back in 1834 a French physicist, Jean Peltier, noticed that if direct current was passed through a circuit composed of two different conductors, say iron and bismuth, a quantity of heat was absorbed at the junction of the two metals. For a long time this phenomenon, which came to be known as Peltier effect, found no practical application, since the cooling registered at the junction was quite insignificant. More than a hundred years later the famous Soviet physicist, Abram Ioffe, suggested that the metals in thermoelectric devices should be replaced by semiconductors, in particular, by compounds of bismuth, tellurium, selenium and antimony. It was then found that Peltier effect could be an effective means of cooling. It proved possible on that basis to develop a new type of refrigerator in which not liquids or gases played the role of coolant but electrons. Tiny electron refrigerators (not bigger than a thimble) lower the temperature to minus 50°C. Another striking feature of such devices is that if the direction of the current is changed they become heaters.

Bismuth compounds are applied in various fields of modern technology: bismuth trioxide serves as a catalyst in the production of acrylic polymers; in the manufacture of glass, enamel and china. This compound is used as a flux lowering the temperature of melting of some inorganic substances; introduced in glass, bismuth compounds increase its refractive index; salts of bismuth are added to paints used for road signs, owing to which they "flare up" when caught in the head-lights; and finally, bismuth salts give lipstick a pearly gleam.

During the last few years scientists have given special attention to superconductivity, a phenomenon discovered in 1911 by a Dutch physicist, Kamerlingh-Onnes and until recently considered to have only theoretical significance. Superconductivity, characterizing some metals, consists in electrical resistance abruptly becoming vanishingly small when the temperature of a metal is close to absolute zero. The rapid development of science and technology in the second half of

this century has revealed wide-ranging prospects for practical uses of superconductivity, and particularly in the power industry. But for these prospects to become reality scientists must find a way of "raising" transition temperature (i. e. the temperature at which superconductivity sets in) as much from the absolute zero as possible. In other words, they must create what can be termed high-temperature superconductors, or materials acquiring superconductivity at more or less tangible temperatures. Some specialists believe that polymers "stuffed" with minute metal particles can be turned into such materials.

Not long ago Soviet chemists achieved the first breakthrough in the solution of this problem. By electrolyzing a water solution of the salts of lead and bismuth over a toluene solution of polydiphenylbutadiene, they obtained a polymer containing nearly 80 per cent of dispersed particles (a few microns in diameter each) of a lead-bismuth alloy. Since the metal became imbedded in the polymer the moment it was formed from the salt, without having become oxidized, the surface of the particles was almost ideally clear. Experiments have shown that the temperature of transition into a superconducting state of the new material is substantially higher than that of the pure alloy, although it is still far from desirable. It is to be hoped that further steps in this research will solve the problem.

Workers at Michigan University (USA) also have some interesting results to their credit. They have established that bismuth "polluted" with a small quantity of atoms of tin or tellurium acquires superconductivity at 0.03 to 0.06 K, while the pure metal is not characterized by this property. By changing the concentration of the addition, it is possible to change bismuth's transition temperature either way.

However, bismuth plays its most important role, that of the heat transfer agent in nuclear reactors, not as a chemical compound or alloy, but in its pure form. This is explained by the wide temperature range in which it remains liquid (melting point 271°C and boiling point 1 560°C), combined with high chemical resistance, and most important of all, with an ability to disperse thermal neutrons practically without absorbing them, that is, without slowing down the chain reaction. Very promising is the use of bismuth in reactors fueled by uranium dissolved in molten bismuth.

Among other distinguishing features of bismuth is that unlike other metals it is very brittle and easily ground into powder. At the same time thin bismuth wire and bismuth plates can be obtained by hot extrusion and compaction. Owing to certain peculiarities of its crystalline lattice, bismuth does not shrink on solidification like most other metals, but expands in volume (just as water does when it freezes). As a rule, the melting point of substances rises if pressure is increased, but with bismuth it is the other way around: the higher the pressure the faster it transforms into liquid state.

Bismuth demonstrates the highest degree of diamagnetism: placed between the poles of a standard magnet, it is repelled from each of them with equal force and comes to rest at a point situated at an equal distance from them. In a magnetic field bismuth's electric resistance grows more than that of other metals. This property is used for measuring induction of strong magnetic fields which is done by means of a bismuth spiral. The electrical resistance of bismuth drops by half when it is melted, and when it is cooled it rises sharply (if the temperature is lowered from zero to minus 180 the resistance goes up 60 times).

As far as the chemical properties of bismuth are concerned, they are close to those of antimony and arsenic — bismuth's neighbours in the 5th group, or more exactly, in its subgroup to the right in the elements table. The difference is that its metallic properties are more pronounced, which is only natural considering its position in the elements table: it is situated closer to the lower left corner — the "metallic pole" of the elements. In a dry atmosphere bismuth is stable, but in a humid one it becomes enveloped in a very thin film of oxide. Heated to over 1 000°C, the metal burns up with a pretty bluish flame.

For almost a hundred and fifty years since Michael Faraday established the main laws of electrolysis, it was believed that during electrolysis the ions of a metal transferred from the anode onto the cathode. In 1975 researchers at the Institute of General and Nonorganic Chemistry of the Ukrainian Academy of Sciences discovered that in the case of some metals the ions during electrolysis head for the anode. The cathode in the Ukrainian scientists' experiment was prepared from bismuth and the anode from nickel, while molten sodium hydroxide was the electrolyte. When electric current was passed through the electrolyte, the bismuth cathode began diminishing fast, and soon after, shiny beads of pure bismuth had settled on the surface of the anode.

However, that discovery did not disprove Faraday's law but rather elucidated it. For it is true that most metals really settle on the cathode, while bismuth, lead, tin and antimony can be exceptions, but only on condition that the electrolyte is a melt of salts of alkali and alkali-earth metals.

The "correction" to the Faraday law can be used to purify many metals and alloys from admixtures of bismuth, lead and other "pollutants". For this, the cathode is made from the metal to be purified and in the process of electrolysis the admixtures isolate themselves from the bulk of the metal and settle on the anode. This method, called cathode cleaning, is very economical.

All metals and most solids, generally, have a definite crystalline structure in which the atoms are situated in a strict order. Not so with liquids and gases. Take water, for instance. Normally, it is an utterly chaotic jumble of H_2O molecules. But once the water is cooled to 0°C, the molecules take up positions, strictly corresponding to the crystalline lattice of ice. Thus, an inconspicuous rain droplet transforms into a beautiful snow-flake. The transformation of a substance from its liquid to solid state is accompanied not only by outward changes but also by changes in many physical and chemical properties.

Not all substances, however, have a crystalline structure. Glass for example, is amorphous both in liquid and solid states. Is it possible to make amorphous metallic melts solidify without acquiring a crystalline structure, that is, produce "metal glass?" It was not idle curiosity that prompted scientists to raise this question: new materials could be expected to demonstrate unique properties. But how could this task be accomplished?

The process of crystallization takes time, during which the molecules of a substance pass through an intermediary phase before taking up stable positions and forming a crystal lattice. So the scientists were faced with the need to attempt to accomplish instantaneous solidification, by-passing the intermediary phase.

A deep vacuum and freezing temperatures were found to be adequate to achieve an immediate transformation of liquid into solid metal. Scientists proved that if metal vapour was directed on a metal placed in a chamber where the two physical conditions were maintained, a "glass" film would immediately be formed on the plate. One experiment involved bismuth and it was found that a film of bismuth "glass", a few microns thick, was characterized by incredible magnetic and superconducting properties. Even at ordinary temperatures its electrical resistance was many times lower than that of bismuth in its crystalline form.

Magnetism and superconductivity are but two crucial properties of materials without which the development of many areas of modern technology is inconceivable. This is why engineers set great store by the metal "glass" ("glass" metal if you will).

Bismuth is the last practically non-radioactive element in the periodic table. We say "practically" because some subtle experiments have demonstrated that the nuclei of its main natural isotope, bismuth-209, are subject to radioactive transformation, although its half-life is hundreds of millions of times greater than the age of the Earth. This is why it is characterized as stable, something which cannot be said about its other 19 isotopes: the half-life of any one of them is no more than a few days.

A fairly recent development in science was the synthesis of the 107th element with the help of bismuth. A bismuth target placed in an accelerator was subjected to a fierce bombardment by ions of chromium. For two months the accelerator operated non-stop and simultaneously the results of dozens of sophisticated experiments were analyzed and compared. It was finally established that the merging of an ion of chromium and a nucleus of bismuth produced the nucleus of the 107th element with a half-life of about two-thousandths of a second.

The demand for bismuth has been growing every year, with the result that the price of this metal on the world market has risen 6 times during the last forty years. In its reserves in the earth's crust bismuth is somewhere in the 8th dozen, behind most rare and trace elements. At the same time it has more than 70 native minerals. True, there are no appreciable concentrations and the metal is obtained as a by-product of lead, copper, silver and other widespread metals, whose ores contain at times as little as 0.0001 per cent of bismuth. It is mostly produced from ores occurring in Bolivia, on the island of Tasmania and in Peru.

In Russia prospecting for bismuth was started during the First World War when the need for bismuth-based therapeutic and anticeptic preparations was particularly acute, and when it became no longer possible to import them from Germany. The Russian Army Sanitary and Evacuation Department requested the Academy of Sciences to find out if bismuth ores occurred in Russia, and if so, whether it would be possible to obtain the metal from them.

The request was passed over to V. I. Vernadsky, the leading Russian geologist who was then head of the Commission for the Study of Russia's Natural Productive Forces. Vernadsky made a careful study of relevant mineral specimens at the Mineralogical Museum of the Academy and arrived at the conclusion that prospecting should be started in the Trans-Baikal area. Soon K. A. Nenadkevich (subsequently a corresponding member of the USSR Academy of Sciences), one of Vernadsky's pupils, set out to Lake Baikal. His search was successful and a while later he reported finding a new mineral (he called it baso-bismuth) in Mount Sherlovaya. The mineral had a rather high concentration of bismuth and could serve as an excellent raw material for bismuth production. Later the scientist found several more bismuth-containing minerals and in 1918 smelted the first few dozens of kilograms of bismuth from one of them found at the Bukuka deposit.

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THE RAREST OF THE RARE (FRANCIUM)

There is always an exception to the rule.— The long wait.— Where is the tenant?— Some forecasting.— Two lines of research.— Unforeseen radiation.— On the shores of the Dead Sea.— In cigar ash.— Discoveries are disproved.— The search continues.— Forked radioactivity.— The vacancy is filled.— A short life.— Physics helps chemistry.— In the process of nuclear bombardment.— Alchemists would be horrified.— The gold that was not needed.— Only one lamp flares up.— Chemistry on the run.— Wide-ranging melting point.— The ice has broken up.

There is always an exception to the rule, and if we accept the rule to be that scientific discoveries are made by men then the exception will be the names of three outstanding women — Marie Sklodowska-Curie, the discoverer of polonium and radium, Ida Noddack, the discoverer of rhenium, and Marguerite Perey, the discoverer of francium.

For 70 years had scientists around the world waited for the birth of No. 87 (the place of francium in the elements table), and there were good reasons for it. When Dmitri Mendeleyev was working on his periodic system not all elements had been discovered and, naturally, he could not fill all the vacancies in his table. But the great scientist was confident that those vacancies were temporary, as the elements to fill them definitely existed in nature but somehow managed to avoid being noticed. Mendeleyev not only assigned them places in his table but also predicted their physical and chemical properties with great accuracy.

Developments were soon to confirm Mendeleyev's scientific acumen: in 1875 gallium was discovered (Mendeleyev had called it eka-aluminium, justly expecting it to resemble its neighbour above in the elements table), 1879 saw the discovery of scandium (eka-boron) and in 1886 came the turn of germanium (eka-silicon).

In his article "The Natural System of Elements and Its Use to Indicate Properties of Undiscovered Elements," published in 1871, Mendeleyev wrote: "Furthermore, we can expect to find some major elements of the 1st, 2nd and 3rd groups in the 10th row; the first must form an oxide of the R_2O type, the second of the RO type and the third of the R_2O_3 type; the first will have similarities with cesium, the second with barium and all their oxides must be strongly basic."

Years passed, more and more elements were discovered but square No. 87 asigned for eka-cesium remained empty despite numerous attempts to find its legitimate tenant. Although this mysterious element managed to remain incognito, scientists had already learned many of its properties determined by its position in the table of elements.

One of the established facts was that this element had to be alkaline, a property that increased in elements the further they were situated from lithium and the closer to cesium. Owing to this fact, it had to be highly reactive (more so than cesium), which was why it could exist in nature only in the form of salts that were to be more soluble than all the other salts of alkali metals. Since the melting point dropped in metals the further they were removed from lithium (from 180.5 to 28.5°C), eka-cesium could be expected to remain liquid, like mercury, under ordinary conditions. Another property typical of alkali metals (except lithium) is that the greater the mass number of an element (that is, the lower it is situated in the elements table), the smaller its content in the earth's crust. Considering that already cesium has very few atoms in nature, it is clear that element No. 87, situated beneath it, had to be the rarest of the rare elements. Finally, the radioactivity of its neighbours on the right (elements mentioned by Mendeleyev in his article) — radium and actinium discovered at the end of the 19th century — gave every reason to suppose that eka-cesium would also be radioactive.

The properties of element No. 87 determined two directions in the search for it: some scientists hoped to find it in the minerals of the alkali metals or in mineral waters and in seas rich in such metals; others preferred to look among the products of radioactive decay of elements neighbouring on eka-cesium.

In 1913 a British radiochemist, Cranston, detected a weak alpha-radiation (along with beta-radiation typical of it) in an isotope of actinium, and suggested that an isotope of element No. 87 could be formed in the process of nuclear disintegration. A year later similar results were reported by the Austrians Meyer, Hess and Paneth. Discovering some "uninvited" alpha-particles in experiments with an isotope of actinium, they wrote that "these particles are formed in the process of alpha-decay of

the usually beta-active actinium-227... The product of the decay must be an isotope of element No. 87." But a suggestion is not yet a scientific fact, especially since there were ample reasons to call it into question: first, the alpha-radiation was too weak to be considered outside the limits of permissible experimental faults and second, the isotope of actinium under study could well contain admixtures of protoactinium occurring alongside it in nature and also characterized by alpha-radiation. Even though those scientists were following a correct path, as was found later, it was still 25 years before the discovery of element No. 87.

In 1925 a British researcher, Friend, set out for Palestine intending to study the water of the Dead Sea rich in alkali metals. He was positive that if eka-cesium could be stable, it was bound to be contained in the water of the Dead Sea. The scientist's supposition was quite logical but no matter how hard he tried to detect No. 87 by X-ray spectroscopy, he failed to observe even traces of it.

The spectroscopic method was used by other scientists as well. It seemed promising since it was this method that had been responsible for the discovery of rubidium and cesium — the closest relatives of No. 87 in the alkali group. Not only concentrates of salts from sea water, but also grains of the rarest minerals, ashes of mushrooms and cigars, burnt sugar and bones of extinct animals — all potential carriers of atoms of eka-cesium became the objects of spectroscopic examinations, but none of them produced the desired results.

Many a time the scientists taking part in the search for eka-cesium announced success only to be disappointed soon after. In 1926 chemical journals reported the findings of the British chemists Drews and Loring who claimed to have observed the lines of the 87th in an X-ray spectrum of the sulphate of manganese. They gave it the name alkalinium. Three years later an American physicist, Allison, published the results of his magnetooptical observations which yielded, as he believed, traces of the element in question in the rare minerals of alkali metals, namely, in samarskite, pollucite and lepidolite. He also proposed that the element be called virginium in honour of his native state. In 1931 his compatriots Papish and Weiner seemed to have confirmed spectroscopically the presence of virginium in samarskite but it was soon found that the foreign lines in the spectrum were due to a defect in the calcite crystal in their spectroscope.

In 1937 a Romanian chemist, Hulubey, announced that he found ekacesium in pollucite and proposed that it should be given the name moldavium. Alas, neither alkalinium, nor virginium, or moldavium was destined to take up the vacant square No. 87 in the periodic table.

Supporters of the radioactive theory were also continuing their search. Back in 1925 D. Dobroserdov, a chemist from Odessa, a Ukrainian town on the Black Sea, published an article in the *Ukrainian Chemical Journal* in which he analyzed some chemical and physical properties of eka-cesium and stressed that the element "had to be highly radioactive". But he mistakenly supposed that the radioactivity of potassium and rubidium was caused by admixtures of element No. 87 which, he suggested, should be called russium if it were to be discovered by Russian scientists.

A year later interesting results were obtained by the well-known radiochemists Hahn of Germany and Hevesy of Hungary. Their study of the radioactive series of some isotopes of actinium demonstrated that the alpha-decay of one of them produced an isotope of eka-cesium, though in a million atoms of the basic substance it was possible to find just a few atoms of the 87th.

Such was the state of affairs in science in 1938 when the search for eka-cesium was joined by Marguerite Perey, a pupil of Marie Sklodowska-Curie and an employee of the Radium Institute of Paris. First she decided to repeat the past experiments of Meyer, Hess and Paneth, for it is often true that the new in science is a long-forgotten old. And so it was with element No. 87.

Just like her predecessors, Perey discovered the presence of alpha-particles. Now her task was to prove that the alpha-source were not admixtures of protactinium but of actinium.

Carrying out a painstaking purification of actinium from all possible admixtures and products of radioactive disintegration, Perey obtained the purest specimen of actinium and found that the isotope of this element with the mass number 227 had a "radioactive fork", in other words, could disintegrate along two lines, emitting beta- and alpha-particles. True the prongs of this fork were not at all equal: it was only in 12 cases out of one thousand that the nuclei of actinium radiated alpha-particles, while in all the other cases they radiated beta-particles (electrons), transforming into the nuclei of an isotope of thorium. But what happened in the process of alpha-emission?

Perey's calculations showed that on ejecting an alpha-particle (i. e. a nucleus of helium), a nucleus of the isotope of actinium lost exactly as much "weight" as was sufficient for it to transform into a nucleus of an isotope of No. 87. She then obtained practical confirmation of the fact that her experiments yielded the product of decay of actinium with typical characteristics of a heavy alkali radioactive metal. That was the long-awaited eka-cesium, or more correctly its isotope with the mass number 223, which had never been found in nature. That was also the last preuranic element and the year of discovery was 1939. Marguerite Perey gave it the name francium in honour of her homeland.

Why had francium succeeded in evading discovery for such a long time? First, because it is the least stable element in nature (with the exception of the transuranic elements). The half-life of its longest living isotope (the one discovered by Perey) is a mere 22 minutes. Is it at all surprising then that practically no traces of francium occur naturally, let alone any appreciable reserves? And yet atoms of francium do exist. Proceeding from the law of radioactive disintegration, scientists have calculated that to every $5976 \cdot 10^{18}$ tons of terrestrial material there is a little more than... 500 grams of francium. So looking for francium is the same as looking for a needle in a heystack. But even so scientists today have some knowledge of francium's physical and chemical properties.

To gain that knowledge they had to obtain artificially an appreciable quantity of the element, carefully purify it from all admixtures and then carry out the necessary experiments and calculations within the shortest possible period of time.

Initially francium was obtained by various chemical methods, but all of them were extremely complicated and far from perfect. It was only when chemists were helped by physicists that any significant success was achieved. The building of cyclotrons and the development of the ion acceleration technique made it possible to work out certain physical methods of obtaining francium, based on the bombardment of thorium or uranium targets by high-energy protons. That was the method used by the workers at the Institute of Joint Nuclear Research in Dubna near Moscow. There a 15-minute bombardment of one gram of uranium in a synchrocyclotron yielded $5 \cdot 10^{-13}$ gram of francium.

Not much, isn't it? In the case of, say, gold a few trillionths of a gram would not be worth a brass farthing. But in the case of francium they were a whole treasure for science, as they enabled it to fill many gaps in the characteristics of this metal. Understandably, in these circumstances it is impossible to determine experimentally the metal's density or its melting and boiling points, but the information gathered provided a basis for determining these characteristics mathematically.

Another method of obtaining francium is by irradiating targets from lead, thallium or gold with accelerated multiply charged ions of, respectively, boron, carbon or neon. Medieval alchemists would have been horrified to learn that instead of doing business scientists were shooting at gold with some particles in order to transform it into a doubtful element and lose it. But it is precisely this doubtful, or rather unknown, quality that compels scientists to stage more and more experiments to satisfy their curiosity about francium.

What are 20th-century "alchemic" processes? A gold foil, only a few microns thick, placed in a cassette is irradiated by accelerated ions of neon, triggering off a nuclear reaction which produces the isotope francium-212. After a half-hour irradiation the cassette with the gold foil is taken to a laboratory where in a protected cabinet the foil is extracted from the casette by means of mechanical arms. Outwardly the foil looks exactly as before, but in actual fact in contains tens of thousands of francium atoms. Not so many to say the least, but it is a fact that scientists nowadays often have to deal with just a few atoms of a substance. For example, element No. 101 (subsequently called mendelevium) was discovered by American scientists when they had obtained only 17 atoms of it, and not all of them simultaneously, but as a result af about a dozen experiments (each yielding one or two atoms). Considered in this context, tens of thousands of atoms is a whole treasure.

But to obtain francium only signifies the beginning of the real work: it has to be isolated from the gold and cleaned from all fission fragments and then subjected to painstaking examination. All this has to be done at really cosmic speed, because the half-life of the isotope of francium produced during the bombardment of gold is just 19 minutes.

First the foil is dissolved in aqua regia and by means of special "gold collectors" the precious (but in this case quite useless) metal is removed from the solution. The next stage is to confirm that the purpose of the operation has been achieved: electronic instruments working on the labelled atoms method indicate that not a single atom of gold has remained in the aqua regia solution. But there are other admixtures which can distort the picture. And every operation cuts short the time left for the study of francium. The "goldless" solution is then passed several times through a column filled with a substance avidly absorbing all products of nuclear disintegration except francium. After purification has been completed, a drop of the solution is transferred into an indent on a Teflon plate and irradiated by a powerful infrared flux. A few seconds later the drop evaporates leaving atoms of francium on the plate. To confirm the presence of the element the plate is placed in the chamber of a sensitive instrument where a vacuum is maintained and a tiny neon lamp indicates the presence of francium. If only one lamp is lighted, it means that francium is pure. If other lamps flare up, it will indicate the presence of other atoms. The concluding and most demanding stage of the experiment is the study of francium proper. The experimenters now have only a few minutes before the metal will be lost to nuclear decay. Scientists themselves jokingly refer to such experiments as "chemistry on the run".

Numerous experiments and calculations have been carried out since francium was discovered and today the basic physical and chemical properties of this element have been studied. Its density is 2.5 g/cm^3 and boiling point, 620-630°C. As to its melting point, opinions differ. It has yet been impossible to measure it because it is beyond the power of science to synthesize it in any adequate quantity. At the same time it is true that at present radiochemists have learned to work with submicroscopic quantities of matter. But it is also true that the smaller the amount of a substance the lower its melting point (grains of gold, for example, measuring 0.01 of a micron, do not melt at 1 063°C as could normally be expected but at 887°C). Obviously then the results of measuring the melting point of an infinitesimal quantity of francium that can be obtained cannot be accurate.

This is why it is only theoretically that scientists can establish this characteristic of francium, and this is by comparing the properties of other alkali metals, establishing the ties between them and then extrapolating established relationships into an area for which no experimental data have been obtained. But this method does not produce results that are as accurate as those that could be achieved were it possible to employ modern methods of measuring temperatures. Hence the differences stemming from the theoretical propositions on which the calculations are based. One comes across the following values for the melting point of francium in the literature (centigrade): 8, 19, 20, 27, 15 through 23, etc.

Chemically francium is the most active alkali metal. While fluorine, situated in the upper right corner of the Mendeleyev table, is the most striking representative of non-metals, its antipode, francium, can be considered the most metallic of all metals.

But what practical use can this element have? Obviously it is still too early to speak of its commercial application. And yet there are certain signs that it could probably be used in future. The typical radiation of this element, for instance, makes it possible to determine if its "forefather", actinium, is present in minerals. Of doubtless interest for medicine is the fact that francium accumulates in cancerous tissue, and what is especially important, even at the initial stages of malignancy. This fact makes the element a promising aid in the early diagnosis of cancer, as has already been demonstrated by experiments on rats. Obviously it is for the future to reveal the abilities of francium, but that will depend on what scientists can learn today.

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ETERNAL RAYS (RADIUM)

What legends have to tell.— A step to immortality.— Three francs a day.— The task is set.— In a cold laboratory.— The great surprise.— When one is moved by need.— In a Paris backyard.— A present from Bohemia.— A magic kingdom.— Four years later.—"I don't need an order."— A triumph of alchemy?— Becquerel's love and injury.— Miraculous healer.— Kelvin's joy.— Necklaces and laboratories.— A Nobel Prize. Pierre Curie's death.— One gram in a mountain of ore.— When a war is on.— A treasure chest.— Russian radium.— A dancer's disappointment.— The little black notebook.

The history of science is associated with numerous legends about how great ideas were born in great minds and great discoveries were made literally within seconds. Just recall Archimedes and what happened to him when he was soaking in his bathtub. As for Newton, they say it was enough for him to be hit by an apple that fell from a tree to enrich physics with one of its fundamental laws — the universal law of gravitation.

Naturally, all could not have been as simple as that, but the point we would like to make here is that to be able to see something one has to have the eyes to see it with. In other words, people often get hit by falling apples but it was only in Newton's case that the incident led to important results, so much so that it was like a splinter of mountain rock touching off an avalanche.

At times a scientific discovery is preceded by months and years of hard work, of series upon series of experiments, of what really amounts to an epic of heroism. A striking example is the history of discovery and isolation of radium, one of nature's most remarkable elements, by Marie Sklodowska-Curie and her husband Pierre Curie. This is why our story about radium is also a story about the two remarkable scientists and their selfless work for the benefit of science.

...Her train ride was in its third day now. Far behind was her native Poland and hundreds of miles of German soil. Ahead lay Paris. What did the future have in store for her, a modest Polish girl who was going to enter the famous Sorbonne? Her plan was to return home after finishing the university and teach physics at school. No one in the world, the least so she herself, knew that her simple plan was not to come true. Fate commanded differently: having taken the train to Paris, Marie Sklodowska-Curie took her first step on the long and arduous road to immortality, a road that put her name in one row with the greatest names in history.

Her life in Paris had begun. It was still years before general recognition and fame would come to her. Right now she could afford only three francs a day to buy her food, clothes, books and notebooks and pay her rent. Even the omnibus to the university was a luxury and she had to walk there in any weather. To save kerosene for the night she rushed to the Saint Genevieve Bibliotheque when dusk fell and worked there till the closing hour —10 p. m. After that she studied till two in the morning in her tiny room in the attic, lit by a kerosene lamp. For weeks her daily ration consisted of tea and bread and butter, or sometimes, of a bunch of radishes or a handful of cherries.

She finished the course at Sorbonne with honours and received two diplomas: in physics and mathematics. In one of the letters to her brother of that period she wrote: "I can see life is not easy to any one of us. Well, one has to have perseverance, and most important of all, confidence of oneself. One must believe that one is fit to do something and must achieve this something at any cost."

In 1895 an important event took place in Marie's life: she married Pierre Curie, then already a well-known physicist. From now on scientific work became their joint endeavour and the meaning of their life. A little more than three years remained to the discovery of radium.

Even the birth of Irene in 1896 did not distract Marie from her research. She worked in her husband's laboratory and taught at the Sorbonne preparatory physics school. The same year she began to work on her dissertation. Her scientific interest then was the mysterious radiation of uranium and its compounds discovered by Becquerel not long before. Both her husband and she decided to continue their scientific quest in that area.

With the help of an instrument designed by her husband, which could estimate quantitatively the flux of the newly-discovered rays, Marie Curie studied thousands of specimens. She worked in extremely hard conditions, in a damp room not suited for her experiments, and with primitive equipment. On a winter day the following entry, touching in its laconism, appeared in the laboratory diary: "The temperature is 6.25°C!!"

But Marie Curie's persistance was staggering. She would not be put off by difficulties. Hundreds of her experiments with various specimens confirmed Becquerel's theory that pure uranium had greater radioactivity than any of its compounds. But still she continued to examine more and more substances. Finally came the day of the great surprise: two uranium minerals — chalcolite and Bohemian pitchblende — registered a much more powerful radiation on her instrument than pure uranium. The conclusion was self-evident: the minerals contained an unknown element (probably more than one) that was much more radioactive than uranium. Analyzing both minerals literally crumb by crumb, the Curies arrived at the conclusion that they contained two unknown elements. They succeeded in identifying one of them and called it polonium in honour of Marie's homeland.

Another period of enormous exertion followed, and in 1898 the scientists discovered another element which was a million times more radioactive than uranium. Because of its inexhaustible capacity for radiation, they gave it the name radium (from the Latin *radius*, ray).

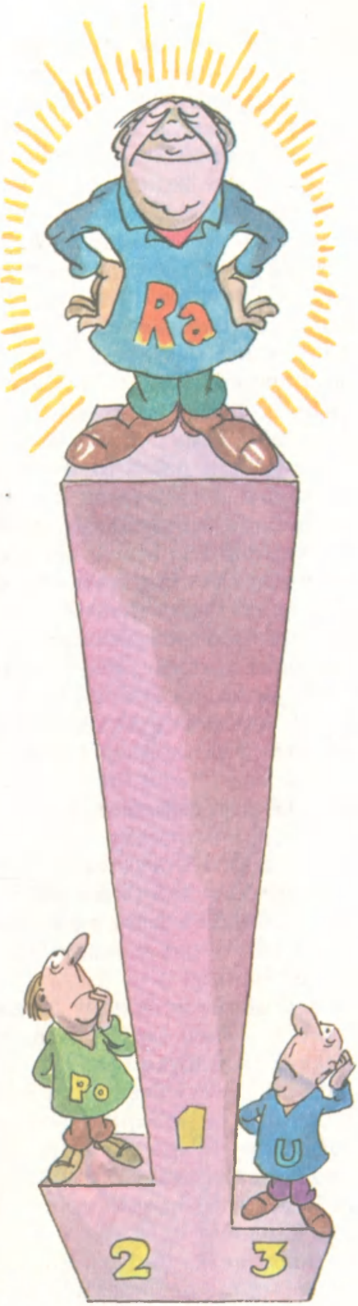
And so polonium and radium were discovered, but no one had yet seen them. The scientists had to work for another four years to be able to demonstrate the two elements to the world.

Only traces of them could be detected in even the most radioactive products. That meant that isolating the two elements would involve processing tons of raw materials and spending a lot of money. Where was it to come from?

The Curies turned to an Austrian physicist asking him to help them buy, at a reasonable price, some waste products of uranium ore, from which uranium was extracted in Bohemia later to be transformed into salts and used as a pigment in the manufacture of glass and porcelain.

In the meantime it was necessary to find adequate premises for the work ahead: the shop where the search for the unknown elements had begun was too small. The board of the Sorbonne refused to help the scientists, saying it "sees no possibility" of placing a laboratory at their disposal. In a neighbouring courtyard the Curies found an abandoned shed, which had the doubtful advantage of being claimed by no one else, and bought it.

Walls made from boards, asphalted ground instead of a floor, a glass roof that leaked when it rained, a few tables roughly knocked together, a stove with a pipe that had rusted through and a blackboard — such was the laboratory in which the physicists had to work over the long years before they succeeded in isolating a few grains of the ra-



diant element. Subsequently Marie Curie wrote: "But it was in that dilapidated shed that the best and happiest years of our life passed, years wholly devoted to work."

While the Curies were busy organizing their new laboratory, good news arrived from Austria: at the request of the Vienna Academy of Sciences, the Austrian government instructed the manager of a uranium ore mine to ship several tons of waste products to Paris.

A short while later, on a fine morning (even if it were showering on that day and the wind were tearing roofs off the houses, Marie would still think it was a fine day) a horse-driven cart stopped at the physics school and, workers began to unload the pile of sacks. Marie could not conceal her joy. She was now the owner of a treasure: the sacks with a dark-brown earth that looked like dust by the roadside concealed her radium. True, to find traces of this metal in a mountain of raw material would really require a great effort, but that did not stop the Curies from getting down to work immediately.

At first they worked together, trying to isolate polonium and radium chemically, but gradually realized that it would be better to divide their responsibilities. Marie continued processing the ores to obtain radium salts and Pierre carried out delicate experiments to determine the properties of the new metal.

There were no exhaust-hoods in the shed to remove the noxious gases released during the processing of ore and more often than not Marie could be seen working in the yard, enveloped in clouds of smoke. But in winter and in bad weather she worked in the shed with the windows open. "I had to process up to twenty kilograms of the stuff a day," she recalled later, "with the result that our whole spacious shed was crammed with large vessels containing residues and solutions. That was back-breaking work — to carry the sacks and the vessels, to pour the liquids from one container into another, and to stir for hours the substance boiling in a cauldron with an iron rod." (When a few years later someone commented on Marie's work in her presence and said it was self-sacrifice, she objected: "What self-sacrifice are you talking about, messieurs, it was all so fascinating!")

And all the while they dreamed of the day when they would see radium with their own eyes, and in their dreams it was beautiful. A few months later they realized that not only was it beautiful, but it constantly radiated light. Every evening as it grew dark they returned to the shed to feast their eyes on the mysterious rays emanating from the radium-enriched substances in the glass vessels and test-tubes crowded on all the tables and benches, to watch how they filled the shed with a magic bluish-green radiance, and how the old walls receded into darkness to make way for the Kingdom of Radium.

Days, weeks and months passed, but the Curies had still been unable to isolate the new metal. There was nothing surprising about it, since the conditions in which the physicists worked were far from adequate, considering the enormity of the chemical problem facing them. There was a moment when Pierre suggested that they should halt the work for a while, get down to theoretical research and wait for better times when it would perhaps be possible to achieve their goal at lesser cost. But Marie was adamant and Pierre gave in.

Finally, the selfless effort bore fruit: in 1902, four years after the Curies announced the possible existence of radium, Marie succeeded in isolating a grain of pure radium chloride which produced a clear spectrum of the new element. The grain was only a fraction of a gram but it was enough for the official recognition of the discovery.

There was no time to be lost and the Curies set out to reveal the properties of their unique element and to see what good it could do. But for that they needed money: their brilliant scientific achievements notwithstanding, money was exactly what they did not have.

They needed a new laboratory to carry out large-scale experiments with the new element, but circumstances were against them. At about this time Pierre Curie's faculty decided to recommend him for the order of Legion of Honour. But this is what Pierre Curie wrote to the dean of the faculty: "This is to request you to convey my gratitude to M. Minister and inform him that I have no need for the order whatsoever but what I do need badly is a laboratory."

But even in their old shed the Curies had made considerable headway in learning more about radium. They found, among other things, that radium not only emitted radiation but also heat: one gram of it released enough heat in one hour to melt one gram of ice.

But over the whole period of its existence (gradually it disintegrates to form other elements) one gram of radium would produce as much heat as is produced in the burning of half a ton of coal, but the period of disintegration would take nearly 20 000 years.

If a pinch of radium salts was placed in a glass tube and sealed and in a few days the air was pumped from it into another sealed tube, the latter would radiate a greenish-blue light in darkness, just like the radium salts proper. This phenomenon attracted the interest of the British scientists, Rutherford, Soddy and Ramsay, who explained that the radiation was

caused by a new gaseous radioactive substance produced by radium. In 1903 they also found that the transformation of radium into the "emanation" (as the gas which was later called radon was referred to) was accompanied by the release of helium, then already a known gas. The work of the British scientists laid the foundations for the theory of radioactive transformations of elements (as a matter of fact radium itself is the product of decay of uranium which was why it was detected for the first time during a study of uranium minerals).

Thus, one element spontaneously transformed into another. Is this fact to be taken to mean that the medieval alchemists' idea of transmutating base metals into gold was not so bad after all? Indeed, it looks like it was not, in principle. But ages passed before mankind's greatest minds proved that such miracles were possible, before they understood why they were possible and learned to accomplish them.

Meanwhile the study of radium in France took a different course: there it became the object of interest of doctors. But before that, it was discovered that radium could cause burns on the human body. To demonstrate that property Pierre Curie held his arm in radium rays for several hours until the skin first became red and then a wound opened, which it took more than two months to heal. Henry Becquerel also got burned by radium, only not willingly. Having carried a test-tube with radium salts in his vest pocket for a while, he suddenly felt an acute burning pain. When he told the Curies about it, he remarked: "I love radium, but it has offended me."

Together with Paris doctors Pierre Curie carried out a series of experiments involving irradiation of animals and obtained astonishing results: radium destroyed malignant cells and cured skin cancer, a disease against which medicine had always been powerless. Soon many patients in Paris hospitals knew from their own experience the miraculous power of radiotherapy.

At the initial stages the Curies supplied doctors with the tubes with the emanation, but the new cancer treatment had won so many advocates in no time that their laboratory could no longer satisfy the growing demand.

The curative properties of radium had by then attracted the attention of industrialists as well. The Curies received a letter from America informing them of plans to build a radium plant in Buffalo and asking for specifications of radium production. The Curies could, of course, have patented their method and thus secured all rights for the industrial production of the element. They could have had considerable financial gain, they needed the money. But being true scientists, they did not believe radium to be their property. They sent a letter to Buffalo containing a detailed description of their method of isolating radium from ores. They were only too glad that more people would soon be able to benefit from the miracle-working rays.

In Europe, too, a plant for the production of radium for medicinal purposes was built by a French industrialist, de Lille, a well-educated man of progressive leanings who even began to publish a journal, *Radium*, wholly devoted to the study of radioactivity.

But all these developments were preceded by some events that played an important role in the life of the Curies. The year 1903 proved a turning point in many respects. In June Marie brilliantly defended her doctor's thesis. A little later the London Royal Society invited Pierre to deliver a report on radium. On arrival in London, the Curies were given an enthusiastic reception. Among the distinguished personalities to meet them was Lord Kelvin. A scientist of world renown, Lord Kelvin was proud to become the outstanding French physicists' friend. The Curies presented him with a glass tube with radium. The great scientist, overwhelmed, did not tire showing the priceless gift to his colleagues.

All the luminaries of British science were present at Pierre Curie's report during which he demonstrated the striking "abilities" of radium: the forces concealed in the element caused a screen, soaked in a solution of zinc sulphate, to shine, they acted on photographic plates wrapped in a black paper, discharged an electroscope at a distance and warmed up the air around it.

Pierre's success exceeded all expectations. The "Professor and Madame Curie" became the focus of attention of aristocratic London. A luxurious banquet was given in their honour, with all the nobility present. The modest couple, not used to such occasions, felt ill at ease in a crowd of high-society people. Marie, who did not even have a wedding ring, was especially self-conscious with all those beautiful ladies around her, dressed up in evening gowns sparkling with fabulous jewelry. At one moment she cast a furtive glance at her husband and was struck to notice that he was secretly observing the ladies' diamonds, pearls and gold, something which was quite unlike him. Pierre explained later: "I didn't know what to do until I thought up a game for myself. I began to count how many laboratories the stones adorning the necks of each of the ladies could buy. By the end of the dinner I had built an astronomical number of laboratories."

A little later the London Royal Society awarded the Curies with the Davy gold medal and in November of the same year (1903), together with Henry Becquerel, they were awarded the highest award that scientists could win — the Nobel Prize. Marie was the first woman in history to become a Nobel laureate. (Eight years later she was awarded for a second time, now for her work in chemistry, and for more than fifty years remained the world's only two-time winner of the Nobel Prize).

The Curies now had everything they could wish for — fame, recognition, and most important of all, the possibility to work in excellent laboratories. But their joy was short-lived: in 1906 Pierre Curie was hit and killed by a dray cart in the street. To somehow alleviate her grief, Marie plunged into the work to which her husband had devoted all his life.

In 1910, together with Andre Debierne, an old friend of the Curie family, Marie Curie achieved an outstanding scientific success: for the first time in history she isolated pure radium (the "radium" produced until then in laboratories and at factories was in fact the chloride or bromide of radium).

The isolation of radium is one of the most complex operations known to chemistry. To obtain one gram of radium it is necessary to process dozens of tons of uranium ore (one ton contains only fractions of a gram), and use up to 500 tons of various reagents, 10 000 tons of coal and as much distilled water. Small wonder then that in 1912 one gram of metallic radium, which outwardly differs little from other metals, cost nearly 500 000 gold roubles. Not a single other substance had over cost so much. This is one case when it would be wrong to say that radium is worth its weight in gold.

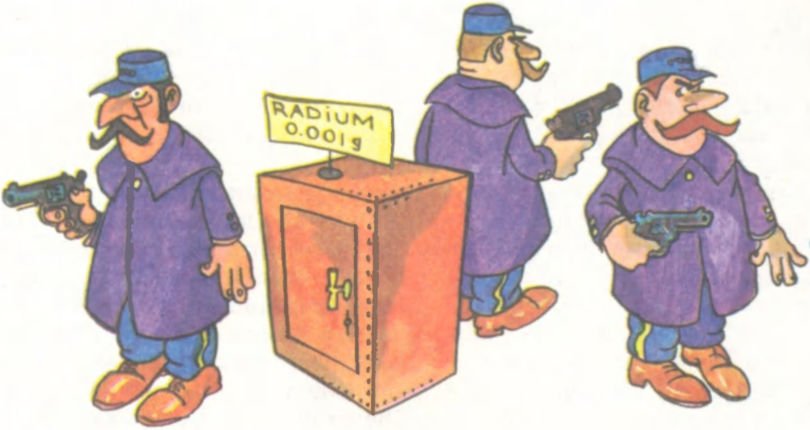
1914 saw one of the Curies' dreams come true: in Pierre Curie Street in Paris the construction of the Radium Institute was completed. It would seem that now Marie had every opportunity to continue the work of her life. But she thought differently: the First World War had broken out and she did not feel she had the right to work in the quiet of her laboratory when there was fire and death around. It was her firm belief that she had to be in the thick of events.

As energetically as during the period she was processing tons of ore, Marie Curie undertook to solve one of the most difficult problems of wartime: to organize X-ray facilities for the wounded not only in hospitals in the rear but also in field conditions. With the money of the Women's Alliance of France she built what was to become the first "radiological automobile" in history. Then came a second, third and a twentieth one. The vehicles travelled all over the front area, stopping wherever the fiercest battles were fought. Marie herself was busy examining the wounded from morning till night, forgetting to eat and sleeping wherever she could — in a nurse's room, in a field tent, or in the open air.

When peace was restored Marie returned to the Radium Institute. She had new plans for research, but for that she needed radium. All she had at her disposal was a little more than one gram of it.

In the spring of 1920 a well-known American journalist, Mrs. Meloney, visited the Radium Institute and interviewed Marie Curie. She asked the scientist what she would have if she were offered to choose from anything she wanted. "I would like," Marie replied, "to have one gram of radium to continue my research, as I cannot afford to buy it."

Anxious as Mrs. Meloney was to help the French scientist, she did not have the necessary 100 000 dollars, either. But she thought up a daring plan: let her fellow-countrymen buy Madame Curie the gram of radium. Back in New York the ingenious journalist started a feverish activity:



she set up a special committee and organized a nation-wide campaign to raise money for the Marie Curie Radium Fund. It was not quite a year later when Marie received a wire from New York informing her that the money for radium had been collected. She set out to Washington and on May 20, 1921, President Harding received her to present her with the radium. True, it was not yet the metal itself, but a small lead-bound chest in which the tubes with the element were to be kept. She was told that radium had been produced for her at a factory in Pittsburgh from where it would be sent to France. The President also gave Marie a scroll of parchment tied with a three-coloured ribbon and put a moire ribbon over her neck with a gold key to the chest on it.

On the eve of the ceremony Mrs. Meloney called on Marie to agree with her on the dedicatory text to be written on the parchment. Marie was resolutely opposed to it: "This document must be changed," she said. "The radium America is presenting me with must always belong to science. I will use it only for scientific purposes as long as I live. But if the text is left as it is, then after my death radium will be inherited by private persons — my daughters. This is impermissible. I would like to give it to my laboratory." And the text was changed.

The interest in radium around the world was great. Even during Marie Curie's lifetime radium institutes were inaugurated in Vienna and Warsaw. At the beginning of 1922 a radium institute opened in Petrograd and was headed by Academician Vernadsky. Addressing one of the sessions of the Russian Academy of Sciences, Vernadsky said: "I'm happy to inform the Academy that this year the staff of the Radium Institute working under V. G. Khlopin succeeded in obtaining the first samples of radium from a Russian ore... The ore was mined in the Ferghana valley (Turkestan, now Uzbekistan). Work is under way not on paper but in reality, and today the first Russian radium has been obtained from a new ore and by a new process."

By 1916 only 48 grams of radium had been produced in the world and about 340 grams by 1927. Even today the world's total reserve of this metal is hardly more than three kilograms. This is only natural: the laboratories, medical institutions and industry — all use radium compounds and not the pure metal, as it is much simpler, hence incomparably cheaper, to produce them.

The element is so powerful that even tiny amounts of its salts added to special paints and pigments are enough to make them luminescent practically for all time. Such paints had been used for a long time on the tips of needles in aircraft instruments to make them visible in darkness.

It is an interesting fact that the idea to use radium for its luminescence occurred for the first time to a well-known American dancer, Loie Fuller. When she learned from a newspaper item that radium emitted light, she decided to make herself a costume with wings that would shimmer when she appeared on a dark stage. She wrote to the Curies but they had to disappoint her: her plan was absolutely unfeasible since the amount of radium required would present grave danger to the dancer's life.

Thus, radium known for its amazing healing properties can also kill if its concentration exceeds a certain permissible level. But what is the permissible concentration? A mere 10 milligrams per cubic kilometre of air. This is why the strictest precautions must be observed during work with this element, and also why of late measures have been taken to replace it in all spheres of science and technology with less dangerous and cheaper artificial radioactive substances.

In 1958 visitors at the Brussels World's Fair were attracted by an exhibit which at first glance did not seem remarkable in any way: an inconspicuous black calico-bound notebook opened at random. That was the laboratory diary of Pierre and Marie Curie. Beside it was a Geiger counter connected to a loudspeaker. It was clicking rhythmically, not stopping for a second. That meant that the notebook was continuously emitting radioactive rays: more than fifty years before a few drops of a solution containing radium salt had been spilled on it by accident.

Those who kept the diary have long been dead. The pages have yellowed and become frail with time, but the clicking of the counter continues. Ages will pass before the radium which was once brought to life in a makeshift laboratory in a Paris yard will finally disappear from the face of the earth. But even ages will not erase the memory of two remarkable people who made one of the greatest discoveries in history.

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