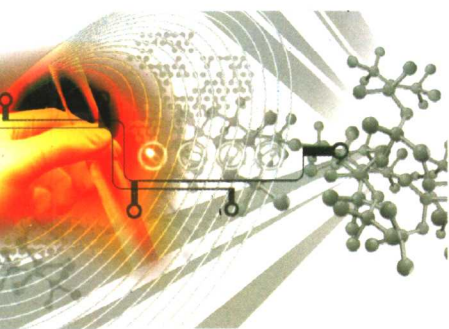



化学原理与热点

CHEMICAL PRINCIPLES AND FOCUSES

主编 ● 郑洪河 赵 扬 卓克垒




 郑州大学出版社

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■ 前 言

经过 200 多年的发展,化学的世界精彩纷呈。当今的化学不仅使人们能够在原子、分子水平上研究物质的组成、结构、性质,从而研究分子和创造分子,而且能够在超分子范畴内新物质和新材料的设计。迅猛发展的化学已经为生命科学、材料科学、环境科学、能源科学、信息科学等领域的突破提供了重要的科学和技术支撑,化学本身也正在解决人类社会的发展过程中面临的环境与能源等重要问题,在提高人类的生活质量、促使人与自然和谐相处等方面发挥着前所未有的重要作用。

立足于现代化学和未来发展的需要,着眼于提高化学专业人员的科学素养,构建“知识与技能”、“过程与方法”、“基础与前沿”相融合的化学体系,我们以化学原理为立足点,以当今化学的热点为重心,以英文的表达方式编写了此书,以期及时反映人类面临的与现代化学相关的原理与热点问题,提高化学工作者的英文能力,促进化学科学的普及和发展。为了保证语言规范和贴近英语表达习惯,本书尽量参考英文原版的资料。该书可以作为在校化学专业的本科生和研究生的学习和参考用书,同时对从事化学研究和开发的专业人员和高等院校的化学教师具有很好的参考和阅读价值。

本书的主要工作是在国家自然科学基金(20573033, 20673033)、河南省杰出青年科学基金(04120001100)、河南省高等学校杰出科研人才创新工程基金(2004KYCX011)、河南省高校创新人才培养工程基金、河南省高校新世纪优秀科研人才支持计划、河南高等教育教学改革研究省级重点项目和河南师范大学教学研究基金重点项目的支持下取得的,本书的出版得到了河南师范大学优秀学术专著出版基金的支持,在此一并表示衷心的感谢!

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由于时间仓促,编者知识水平有限和经验不足,肯定存在许多不足之处,敬请国内外同行批评指正。

编者

2007 年 2 月



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■ Topic 1

About Chemistry

Alchemy

Alchemy is the origin of chemistry. The predecessor of chemistry, practised from as early as 500 BC through the 16th century. Its two principle goals were transmutation of the baser metals into gold and discovery of a universal remedy. Modern chemistry grew out of alchemy by gradual stages.

What is Chemistry?

Chemistry is a basic science whose central concerns are:

1. The structure and behavior of atoms (elements);
2. The composition and properties of compounds;
3. The reactions between substances with their accompanying energy exchange;
4. The laws that unite these phenomena into a comprehensive system.

Chemistry is not an isolated discipline, for it merges into physics and biology. The origin of the term is obscure. Chemistry evolved from the medieval practice of alchemy. Its bases were laid by such men as Boyle, Lavoisier, Priestly, Berzelius, Avogadro, Dalton and Pasteur.

Chemistry is especially connected with learning and understanding the changes that take place between chemicals, changes that we call chemical reactions. In a chemical reaction, chemicals interact with each other to form entirely different substance with different properties. Sometimes these changes can be quite dramatic, as illustrated by the reaction of sodium with chlorine.

Sodium is a metal. Like other metals, it is shiny and conducts electricity well. Unlike other metals, though, it is very soft and is easily cut with a knife. Notice that the outside of the bar of sodium coated with a white film. This is formed by the reactions of sodium with oxygen and moisture in the air. The tendency of sodium to react rapidly with oxygen and water makes it a dangerous chemical with which to work. Sodium reacts violently in water, producing a lot of heat and liberating the flammable gas hydrogen. In this same reaction sodium also forms a substance called sodium hydroxide, commonly known as lye, which is very corrosive toward flesh. Contacting of sodium with your skin can cause severe chemical burns.

Chlorine is different from sodium in many ways. It is a pale, yellow-green gas. If you have ever smelled a liquid laundry bleach such as clorox, chlorine you have smelled is especially dangerous to inhale, causing severe lung damage that can easily lead to death. In fact, chlorine gas has been used as a weapon of war.

When metallic sodium and gaseous chlorine come together they react violently. The substance formed in this reaction is white powder, quite different in appearance from either sodium or chlorine. Its chemical name is sodium chloride, although it is known to most people by its common name, salt.

If you think about this reaction for a moment, perhaps it will strike you as really quite amazing, and even a bit like magic. Here we have two chemicals, sodium and chlorine, whose ingestion can produce severe medical problems or even death? Yet, when they react with each other they form a substance our bodies cannot do without! Such startling events help make chemistry fascinating. As you study this course, perhaps you will discover for yourself that same sense of magic that has caught the imagination of others and produced generations of chemists.

Most chemical reactions are not quite as spectacular as the one between sodium and chlorine. Nevertheless, they take place in us and around us all the time. We metabolize the foods we consume, while photosynthesis creates their replacements. Chemical reactions in batteries supply us with energy as does the combustion of fuels. Chemical reactions in the air lead to smog, while in the upper atmosphere sunlight interacting with gases released from aerosol cans and damaging air conditioners degrades the natural ozone layer that shields the Earth from harmful ultraviolet. Understanding these reactions and seeking to control the ones that can be harmful to us is an important role for chemistry in modern science and in our society.

As a science, chemistry is a dynamic subject, constantly changes as new discoveries are made by scientists who work in university and industrial laboratories. The general

approach that these scientists bring to their work is called the scientific method. It is, quite simply, a common sense approach to developing an understanding of natural phenomena.

A scientific study normally begins with some observation that fires our curiosity and raises questions about the behavior of nature. Usually, we begin to search for answers in the work of others who have published in scientific journals. As our knowledge grows, we begin to plan experiments that permit us to make our own observations. Generally, these experiments are performed in a laboratory under controlled condition so the observations are reproducible. In fact, the ability to obtain the same results when experiments are repeated is what separates a true science from a pseudoscience such as astrology.

The observations we make in the course of performing experiments provide us with empirical facts—so named because we learn by observing some physical, chemical or biological system. These facts are referred to as our data. For example, if we study the behavior of gases, such as the air we breathe, we soon discover that the volume of a gas depends on a number of factors, including the mass of the gas, its temperature and its pressure. The bits of information we record relating these facts are our data.

One of the goals of science is to organize facts so that relationships or generalizations among the data can be established. For instance, one generalization we would make from our observations is that when the temperature of a gas rises, the gas tends to expand and occupy a large volume. If we were to repeat our experiments many times with numerous different gases, we would find that this generalization is uniformly applicable to them all. Such a broad generalizations, based on the results of many experiments, is called a law or scientific law.

As useful as they may be in summarizing the results of experiments, laws can only state what happens. They do not explain why substances behave the way they do. Human beings are curious creatures, though, and we seek explanations. Therefore, after we have collected and studied our data we begin to speculate about the reasons for the results of our experiments. The tentative explanation we formulate is called a hypothesis. We use hypothesis to make predictions of new behavior and then design experiments to test our predictions. If the results of these new experiments prove us wrong, we must discard the hypothesis and seek a new one. However, if our experiment survives repeated testing, it is gradually accepted and may ultimately achieve the status of a theory. A theory is a tested explanation of the behavior of nature. Most useful theories are broad with many far-reaching and subtle implications. It is impossible to perform every test that may show such a theory to be wrong, so we can never be absolutely sure the theory is correct.

The sequence of steps just described—observation and the testing of an explanation by

additional experiments—constitute the science. An auto mechanic follows the same steps when fixing your car. First, tests are performed (observation) that enable the mechanic to suggest the problem (a hypothesis). Then parts are replaced and the car is checked to see whether the problem has been solved (testing of the hypothesis by experiment). In short, we all use the scientific method as much by instinct as by design.

From the preceding discussion you may get the impression that scientific progress always processed in a dull, orderly, and stepwise fashion. This is not true; science is exciting and provides a rewarding outlet for cleverness and creativity. Luck, too, sometimes plays an important role. For example, in 1828 Frederick Wohler, a German chemist, was heating a substance called ammonium cyanate in attempt to add support to one of his hypotheses. His experiment, however, produced an unexpected substance, which out of curiosity he analyzed and found to be urea (a constituent of urine). This was an exciting discovery because it was the first time anyone had ever knowingly made a substance produced only by living creatures from a chemical not having a life origin. The fact that could be done led to the beginning of a whole new branch of chemistry. Yet, had it not been for Wohler's curiosity and his application of the scientific method to his unexpected results, the significance of his experiment might have gone unnoticed.

As a final note, it is significant that the most spectacular and dramatic changes in science occur when major theories are proven wrong. This happens only rarely, but when it does occur, scientists are sent scrambling to develop new theories, and exciting new frontiers are opened.

Inorganic Chemistry

A major branch of chemistry is generally considered to embrace all substances except hydrocarbons and their derivatives, or all substances that are not compounds of carbon disulfide. It covers a broad range of subjects, among which are atomic structure, crystallography, chemical bonding, coordination compounds, acid-base reactions, ceramics and the various subdivisions of electrochemistry (electrolysis, battery science, corrosion, semiconduction, etc.). It is important to state that inorganic and organic chemistry often overlap. For example, chemical bonding which applies to both disciplines, electrochemistry and acid-base reactions having their organic counterparts, catalysts and coordination compounds may be either organic or inorganic.

Regarding the importance of inorganic chemistry, R. T. Sanderson has written: "All chemistry is the science of atoms, involving an understanding of why they possess certain

characteristic qualities and why these qualities dictate the behavior of atoms when they come together. All properties of material substances are the inevitable result of the kind of atoms and the manner in which they are attached and assembled. All chemical change involves a rearrangement of atoms. Inorganic chemistry is the only discipline within the chemistry that examines specifically the differences among all the different kinds of atoms”.

Organic Chemistry

A major branch of chemistry which embraces all compounds of carbon except such binary compounds as the carbon oxides, the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene (COCl_2), carbonyl sulfide (COS), etc.; and the metallic carbonates, such as calcium carbonate and sodium carbonate. The total number of organic compounds is indeterminate, but some 6,000,000 have been identified and named.

Important areas of organic chemistry include polymerization, hydrogenation, isomerization, fermentation, photochemistry and stereochemistry. There is no sharp dividing line between organic and inorganic chemistry, for the two often tend to overlap.

Analytical Chemistry

Analytical chemistry is the subdivision of chemistry concerned with identification of materials (qualitative analysis) and with determination of the percentage composition of mixtures or the constituents of a pure compound (quantitative analysis). The gravimetric and volumetric (or “wet”) methods (precipitation, titration and solvent extraction) are still used for routine work and new titration methods have been introduced, e. g. cryoscopic, pressure-metric (for reactions that produce a gaseous product), redox methods and use of a F-sensitive electrode etc. However, faster and more accurate techniques (collectively called instrumental) have been developed in the last few decades. Among these are infrared, ultraviolet, and X-ray spectroscopy where the presence and amount of a metallic element is indicated by lines in its emission or absorption spectrum. . . Colorimetry by which the percentage of a substance in solution is determined by the intensity of its colour. . . Chromatography of various types by which the components of a liquid or gaseous mixture are determined by passing it through a column of porous material or on thin layers of finely divided solids. . . Separation of mixtures in ion exchange columns and radioactive tracer analysis. Optical and electron microscopy, mass spectrometry, microanalysis,

Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupole Resonance (NQR) spectroscopy all fall within the area of analytical chemistry. New and highly sophisticated techniques have been introduced in recent years, in many cases replacing traditional methods.

Physical Chemistry

Application of the concepts and laws of physics to chemical phenomena is in order to describe in quantitative (mathematical) terms or a vast amount of qualitative (observational) information. A selection of only the most important concepts of physical chemistry would include: the electron wave equation and the quantum mechanical interpretation of atomic and molecular structure, the study of the subatomic fundamental particles of matter, application of thermodynamics to heats of formation of compounds and the heats of chemical reaction, the theory of rate processes and chemical equilibria, orbital theory and chemical bonding, surface chemistry, including catalysis and finely divided particles, the principles of electrochemistry and ionization. Although physical chemistry is closely related to both inorganic and organic chemistry, it is considered a separate discipline.

Stoichiometry

Stoichiometry is the branch of chemistry and chemical engineering that deals with the quantities of substances that enter into, and are produced by chemical reactions. For example, when methane unites with oxygen in complete combustion, 16 g of methane require 64 g of oxygen. At the same time 44 g of carbon dioxide and 36 g of water are formed as reaction productions.

Every chemical reaction has its characteristic proportions. The method of obtaining these from chemical formulas, equations, atomic weights and molecular weights, and determination of what and how much is used and produced in chemical process, is the major concern of stoichiometry.

Biochemistry

Originally a subdivision of chemistry but now an independent science, biochemistry includes all aspects of chemistry that apply to living organisms. Thus, photochemistry is

directly involved with photosynthesis and physical chemistry with osmosis. Two phenomena underlie all plant and animal life. Other important chemical mechanisms that apply directly to living organisms are catalysis, which takes place in biochemical systems by the agency of enzymes; nucleic acid and protein constitution and behavior, which is known to control the mechanism of genetics; colloid chemistry, which deals in part with the nature of cell walls, muscles, collagen, etc; acid-base relations, involved in the pH of body fluids; and such nutritional components as amino acids, fats, carbohydrates, minerals, lipids and vitamins, all of which are essential to life. The chemical organization and reproductive behavior of microorganisms (bacteria and viruses) and a large part of agricultural chemistry are also included in biochemistry. Particularly active areas of biochemistry are nucleic acids, cell surfaces (membranes), enzymology, peptide hormones, molecular biology and recombinant DNA.

Nuclear Chemistry

The division of chemistry is dealing with changes in or transformations of the atomic nucleus. It includes spontaneous and induced radioactivity, the fission or splitting of nuclei, and their fusion, or union; also the properties and behavior of the reaction products and their separation and analysis. The reactions involving nuclei are usually accompanied by large energy changes, far greater than those of chemical reactions; that are carried out in nuclear reactors for electric power production and manufacture of radioactive isotopes for medical use, also (in research work) in cyclotrons.

■ Topic 2

Inorganic Chemistry and Elements

Mixtures are combinations of two or more pure substances in which each substance retains its own composition and properties. Some mixture which is not uniform throughout, is called heterogeneous. The others which have uniform properties are described as homogeneous.

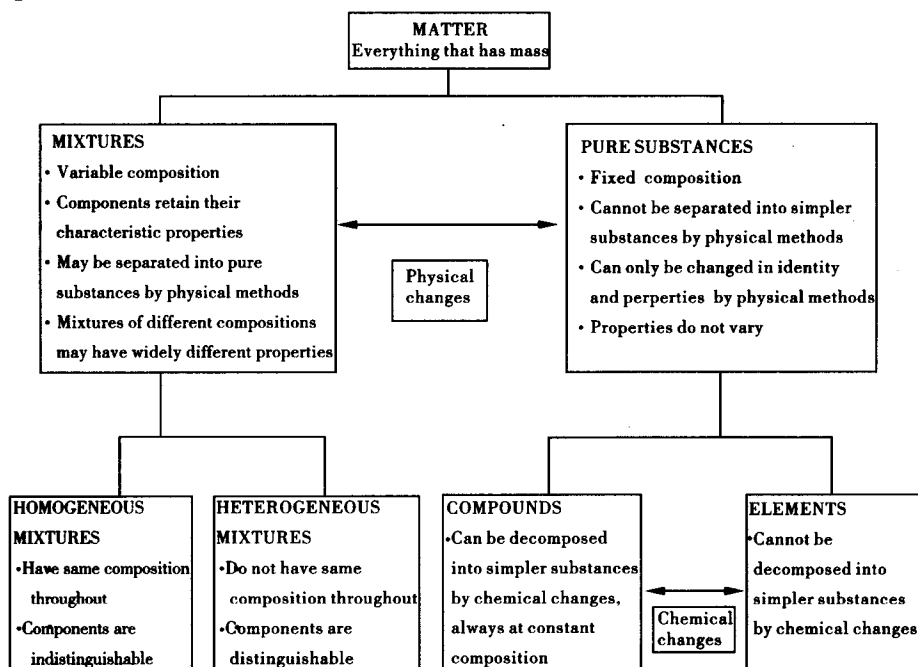


Fig. 2.1 One scheme for classification of matter

Arrows indicate the general means by which matter can be separated

A substance is the basic chemical unit which cannot be further broken down by physical means.

Elements are substances which cannot be decomposed into simpler substances by chemical changes.

The following table explains the classification of matter.

It has been well known that there are more than 100 elements in our world, which can be logically arranged in a periodic table of elements:

1 H																		2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 110	111 111	112 112							

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 2.2 The periodic table of elements

What is the origin of the name of each element? If you were to discover a new element, how would you name it? Throughout history, scientists have answered this question in different ways. Most have chosen to honor a person or a place or to describe the new substance. Even elements known long ago, whose discoverers are unknown, have named with etymological significance. Seen from a historical point of view, these names tell us much about the nature of chemistry and scientific discovery. They also tell us about the nature of scientists—their values heroes and practices. Many elements were unearthed by teams rather than individuals. Chemists of different nationalities or schools who had worked

cooperatively were sometimes reduced to bickering enemies when the time came to choose a name for their discovery!

Until the Middle Ages only nine elements were known: gold, silver, tin, mercury, copper, lead, iron, sulfur and carbon. The metals' chemical symbols are taken from descriptive Latin names: aurum ("yellow"), argentum ("shining"), stannum ("dripping" or "easily melted"), hydrargyrum ("silvery water"), cuprum (Cyprus, where many copper mines were located), Plumbum (exact meaning unknown—possibly "heavy") and ferrum (also unknown). Some of these were derived from even earlier Sanskrit words. The English names are derived from old Anglo-Saxon terms. Mercury is named after the planet, one reminder that the ancients associated metals with gods and celestial bodies. In turn, both the planet, which moves rapidly across the sky, and the element, which is the only metal that is liquid at room temperature and thus flows rapidly, are named for the fleet god of messengers in Roman mythology. In English, mercury is nicknamed "quicksilver".

Prior to the reforms of Antoine Lavoisier, chemistry was a largely non-quantitative, unsystematic science in which experimenters had little contact with each other. There were few rules for documenting and sharing information. Thus, elements discovered prior to Lavoisier's contributions in the late 18th century have names whose sources are hard to identify. They included the following "Zinc" which might have originated from the Persian seng ("stone") or the German Zinke ("spike"). "Antimony" is thought to have come from the Arabic alithmid, the name for the compound Sb_2S_3 , which was used to darken women's eyebrows (its Latin name, stibium, means mark). Arsenic is another element with an ambiguous etymology. The Greek word arsenikos, meaning male, is one possible source, as alchemists believed that metals were either male or female. The Persian zarnik ("golden") is another.

In 1787, Lavoisier published his *Methode de Nomenclature Chimique*, which proposed that all new elements be named descriptively. For the next 125 years, most elements were given names that corresponded to their properties. Greek roots were one popular source, as evidenced by hydrogen (hydros-gen, "water-producing"), oxygen (oksys-gen, "acid-producing"), nitrogen (nitron-gen, "soda-producing"), bromine (bromos, "stink") and argon (a-er-gen, "no reaction"). The discoverers of Argon, Ramsay and Rayleigh, originally proposed the name aeron (from aer or air) but critics thought it was too close to the biblical name Aaron! Latin roots such as radius ("ray") were also used (radium and radon are both naturally radioactive elements that emit "rays"). Color was often the determining property, especially after the invention of the spectroscope in 1859, because

different elements (or the light that they emit) have prominent characteristic colors. Cesium, indium, iodine, rubidium and thallium were all named in this manner. Their respective Greek and Latin roots denote blue, gray, indigo, violet, red and green (thallus means "tree sprout"). Because of the great variety of colors of its compounds, iridium takes its name from the Latin iris, meaning rainbow. Alternatively, an element name might suggest a mineral or the ore that contained it. One example is wolfram or tungsten (W), which was isolated from wolframite. Two other "inconsistent" elemental symbols, K and Na, arose from occurrence as well. Kalium was first obtained from the saltwort plant—*Salsola kali*, and natrium from niter. Their English names, potassium and sodium, are derived from the ores potash and soda.

Other elements, contrary to Lavoisier's suggestion, were named after planet, mythological figures, places or superstitions, and "celestial elements" include helium (sun), tellurium (earth), selenium (moon—the element was discovered in close proximity to tellurium), cerium (the asteroid Ceres, which was discovered only two years before the element) and uranium (the planet Uranus, discovered a few years earlier). The first two transuranium elements (those beyond uranium) to be produced were named neptunium and plutonium for the next two planets, Neptune and Pluto. The names promethium (Prometheus, who stole fire from heaven), vanadium (Scandinavian goddess, Vanadis), titanium (Titans, the first sons of the earth), tantalum (Tantalos, father of Niobe) and thorium (Thor, Scandinavian god of war) all arise from Greek or Norse mythology. Cobalt was named for Kobold German evil spirit, when its presence interfered with the mining of copper (as did nickel, from Kupfernickel, or false copper).

"Geographical elements" shown on the map, sometimes honored the discoverer's native country or workplace. The Latin names for Russia (ruthenium), France (gallium), Paris (lutetium) and Germany (germanium) were among those used. Marie Skłodowska Curie named one of the elements that she discovered polonium, after her native Poland. Often the locale of discovery lends its name to the element; the record holder is certainly the Swedish village Ytterby, the site of ores from which the four elements terbium, erbium, ytterbium and yttrium were isolated. Elements honoring important scientists include curium, einsteinium, nobelium, fermium and lawrencium.

Sometimes the name of an element contains a history of its discovery. In 1839 Mosander gave a new element he had extracted as a minor component in a cerium compounds the name lanthanum (Greek, "to lie hidden"). Two years later he thought that he had found another new element from the same source, and named it didymium (Greek, "twin") because it was "an inseparable twin brother of lanthanum". But in 1885, Von

Welsbach separated didymium into two new elements, which he named neodymium (Greek, “new twin”) and praseodymium (Greek, “green twin”).

Most of the 109 elements now known were given titles peacefully, but a few were not. Niobium, isolated in 1803 by Ekeberg from an ore that also contained tantalum, and named after the Greek goddess Niobe (daughter of Tantalus), was later found to be identical to an 1802 discovery of Hatchett, columbium. (Interestingly, Hatchett first found the element in an ore sample that had been sent to England more than a century earlier by John Winthrop, the first governor of Connecticut.) While “niobium” became the accepted designation in Europe, the Americans, not surprisingly, chose “columbium”. It was not until 1949—when the International Union of Pure and Applied Chemistry (IUPAC) ended more than a century of controversy by ruling in favor of mythology—that element 41 received a unique name. Current arguments over the proper names of elements 104 and 105 have prompted the IUPAC to begin hearing claims of priority to numbers 104 through 110. Some Russian and Scandinavian texts refer to 104 as kurcha-tovium; some American and English texts as rutherfordium. Similarly, 105 is known as both hahnium and nielsbohrium.

In 1978, the IUPAC recommended that, at least for now, the elements beyond element 103 be known by systematic names based on numerical roots.

Elements of atomic numbers of 101 to 103 have trivial names and corresponding two letter symbols approved by IUPAC. The status of these names and symbols is in no way affected by the recommendation of systematic names for elements of atomic numbers greater than 100.

Elements of atomic numbers greater than 103 are often referred to in the scientific literature but receive names only after they have been “discovered”. Names are needed for indexing and other purposes and the Commission on Nomenclature of Inorganic Chemistry was asked to make recommendations concerning names and symbols of the heavy “unknown” elements. The Commission decided that these elements would be best named systematically and that names should accord with the following principles:

(i) The names should be short and obviously related to the atomic numbers of the elements.

(ii) The names should end in “ium” whether the element was expected to be a metal or otherwise.

(iii) The symbols for the systematically named elements should consist of three letters.

(iv) The symbols should be derived directly from the atomic numbers and be visually related to the names as far as possible.