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Dmitrii Ivanovich Mendeleev (1834-1907):

The Periodic Table and Beyond

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Content Highlight: The periodic law of chemical elements is one of the most significant achievements in science. It was discovered by Dmitrii Mendeleev in 1869, and 2019, the year of its 150th anniversary, was proclaimed the "International Year of the Periodic Table of Chemical Elements (IYPT2019)" by the United Nations General Assembly and UNESCO. In this article we briefly outline the Mendeleev's path to the discovery and present a broader perspective of his views and research, including less known accomplishments such as theory and investigations of solutions, studies of gases, and the discovery of supercritical fluids. We also find very instructive some "delusions of genius", his path to fame and consider several myth, broadly circulating in media and widely accepted by public.

2019 - International Year of Periodic Table

Last year, both general public and international scientific community had a remarkable opportunity to look back to the year 1869, when Dmitrii Mendeleev – see Fig.1 - first proposed the periodic system of the elements, a framework that has truly become a common language for science. In December of 2017, the United Nations General Assembly proclaimed 2019 as "the International Year of the Periodic Table of Chemical Elements [IYPT2019] to enhance global awareness of, and to increase education in, the basic sciences..." to be led by the United Nations Educational, Scientific, and Cultural Organization (UNESCO) [Ref 1].

Mendeleev's table offered a natural classification of the known elements, and his periodic law enabled him to predict those that were missing, along with their physical and chemical properties. His system also paved the way for many other discoveries such as those of the noble gases by William Ramsay and Lord Rayleigh (1904 Nobel Prize in Chemistry) and the first radioactive elements by Marie Curie, along with her husband Pierre (1903 Nobel Prize in Physics, 1911 Nobel Prize in Chemistry).

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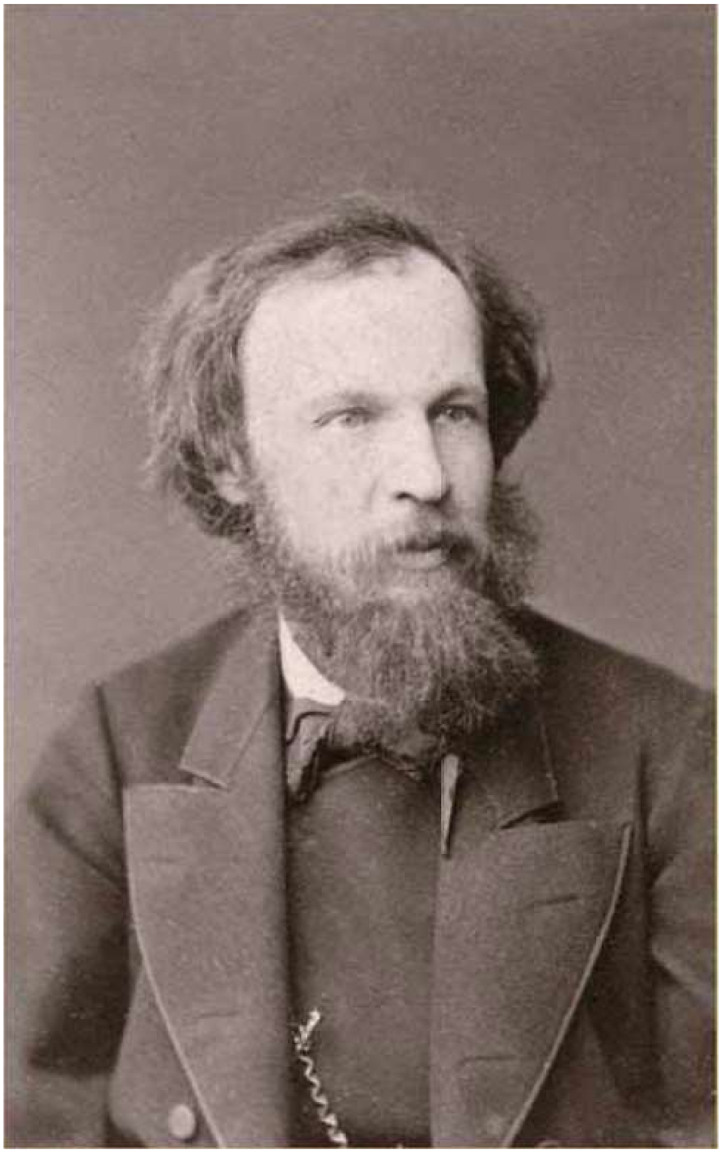


Fig.1: Dmitrii Mendeleev in 1869, the year he formulated the periodic law.

Since mid-20th century, accelerators have started to play major role in filling in the periodic table as we know it now. All but two trans-uranium elements, from Neptunium (93) to Oganesson (118, the last element of nowadays' table), have been discovered at cyclotron accelerator facilities in the US, USSR/Russia, Germany, and Japan. The 1951 Nobel Prize in Physics went to Glen Seaborg and Edwin McMillan for the discovery of transuranic elements, while Ernest O. Lawrence, a pioneer of modern particle accelerators, won the Nobel Prize in Physics in 1939 for his invention of the cyclotron.

In recognition of the 150th anniversary, *Nature, Science* and the *Physical Review* journals have published special issues and article series on various aspects of these discoveries, many of which are available free-to-read at the journals websites [Ref.2].

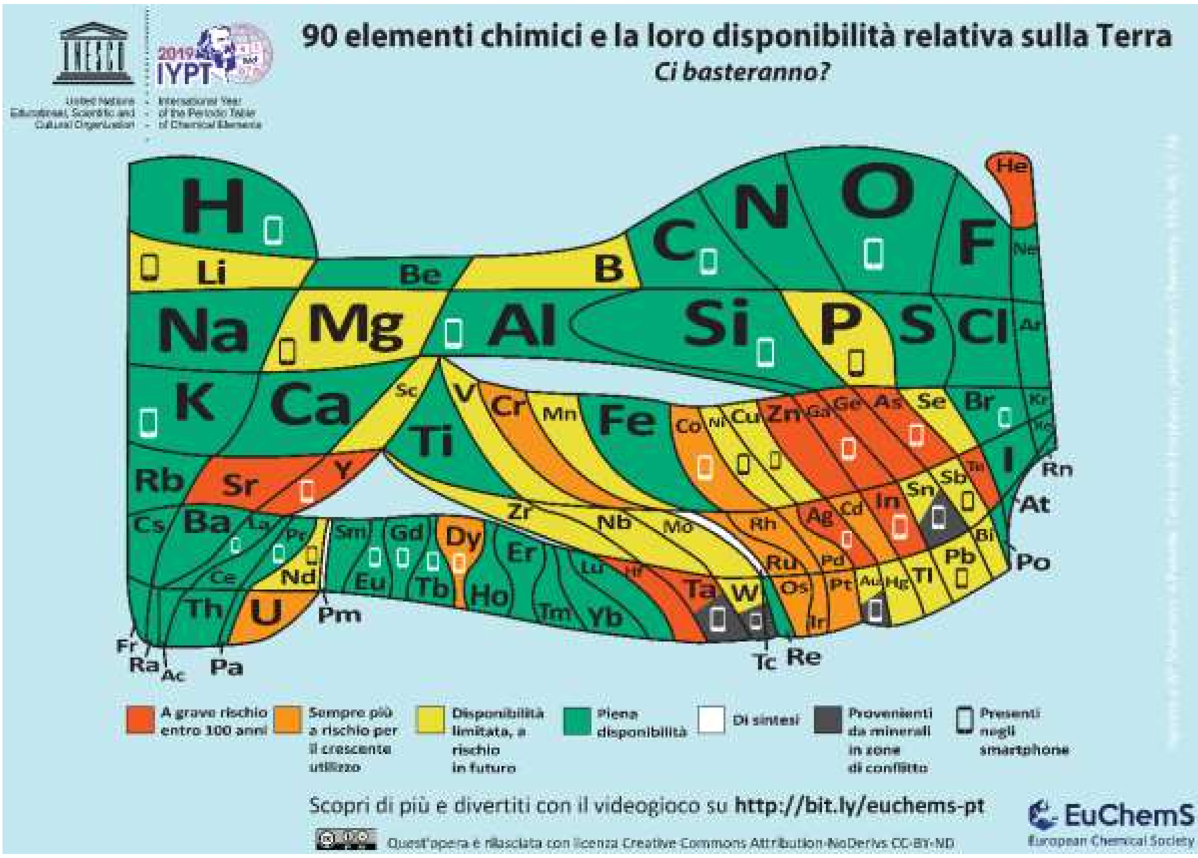


Fig.2: The Periodicd Table presentation developed by the European Chemical Society reflects elements scarcity – "How much is there? Is that enough?" – by color and size of elements boxes [Ref. 3].

The IYPT2019 web site has an impressive map of hundreds of events and celebrations world-wide, organized by various universities, associations, organizations, and institutions. For example, Fermilab and CERN have celebrated the IYPT, organized colloquia, seminars and lectures on the Periodic Law, its history and influence. On September 12, 2019, the President of the European Physical Society (EPS) Petra Rudolf inaugurated the Mendeleev Museum-Archive, at the University of Saint Petersburg as the EPS Historic Site and ceremonially unveiled a commemorating plaque in a ceremony attended by many scientists, chemists and physicists, members of EPS and APS. The European Chemical Society had marked the IYPT with a new look of the Periodic Table that reflects elements scarcity depicted in Fig.2.

Many IYPT commemorating events took place in Italy. Besides several talks and seminars which took place in various institutions, such as the INFN Ferrara and the INFN Padova, the 2019 Festival della Scienza in Genova (October 24 – November 4), a very popular annual public science event, was organized under the main theme of “The Elements” to celebrate the occasion of the IYPT2019. On November 6 and 7, 2019, the Italian Physical Society (SIF) in collaboration with the Italian Chemical Society (SCI) organized “Passion for Science: New Elements and New Materials” - International Symposium on the occasion of the IYPT2019 [Ref.4].

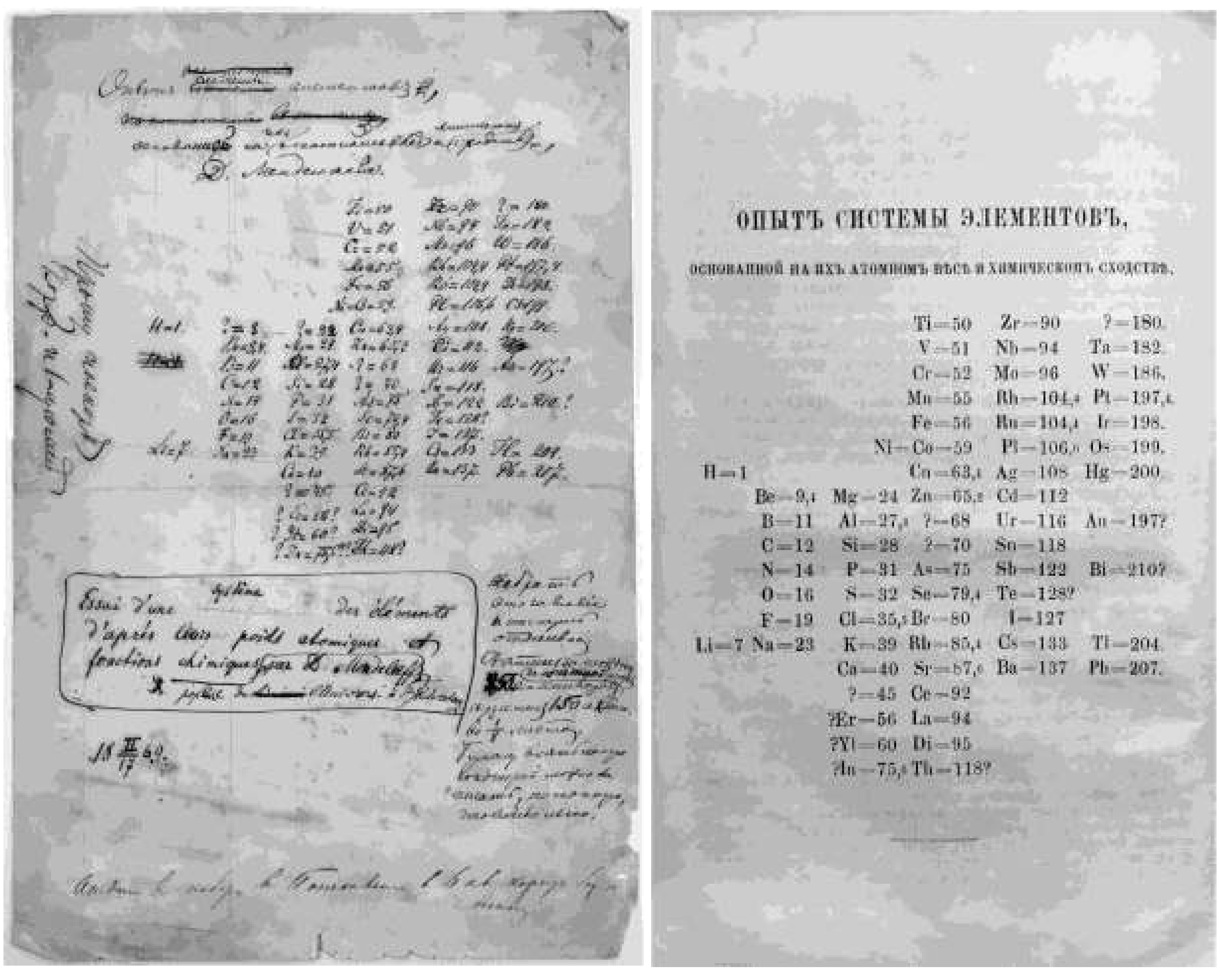
The IYPT celebrations all came to a close at a ceremony in Tokyo on December 5, 2019. Attendees were treated to presentations from representatives of the International Union of Pure and Applied Chemistry and the International Union of Pure and Applied Physics, scientists involved in the discovery of new elements, and observations on what lies in the future for the periodic table.

Mendeleev and His Periodic Law

Mendeleev’s life and his path toward the periodic law are well studied and reflected in many publications (see, e.g., [Refs. 5-8]). Below we give only a short summary and present only either most basic or less known facts of his biography and research. Mendeleev was born in the small Siberian town of Tobolsk some 2300 km North-East of Moscow as the last of 11 surviving children of Ivan Mendeleev, a director of the local gymnasium, and Mariya Kornileva. The father became blind shortly after Dmitrii’s birth and died in 1847. After an unsuccessful attempt to support the family operating a small glass factory, his mother took him to St. Petersburg in 1848, where he enrolled in the Main Pedagogical Institute, which he graduated from in 1855. Despite significant health problems and hardships after the death of his mother in 1850 he received a master’s degree in chemistry in 1856 and began to conduct research in organic chemistry. Starting 1859, Russian government fellowship supported his 22 month study abroad for at the University of Heidelberg. Instead of working closely with the prominent chemists of the university, including Robert Bunsen (now widely known for the “Bunsen burner”) and Emil Erlenmeyer (known for the namesake chemical flask), Mendeleev set up a laboratory in his own apartment to study the molecular mechanics of surface tension. Participation in the 1860 International Chemistry Congress in Karlsruhe, championed by the Italian chemist Stanislao Cannizzaro, allowed him to take part in the discussions on crucial issues such as atomic weights, chemical symbols, and chemical formulas, as well as to meet and establish contacts with many of Europe’s leading chemists.

In 1861 Mendeleev returned to St. Petersburg, where he became Professor of chemistry at the Technological Institute in 1864. After the defense of his doctoral dissertation in 1865 he was appointed Professor of chemical technology at the University of St. Petersburg (now St. Petersburg State University), where he later became Professor of general chemistry (1867) and continued to teach until 1890. From 1893 to his death in 1907, Mendeleev was a director of the Chief Bureau of Weights and Measures, as well as worked as a consultant on a broad variety of business, research and state projects.

The turning point toward the discovery of the periodic law of chemical elements was the need in logical systematization of elements for the textbook "Osnovy Khimii (The Principles of Chemistry)" [Ref. 9], which later became a classic, running through 13 editions in Russia (including 5 post humous ones in the USSR) and many translations to English, German and French. As Mendeleev began to teach inorganic chemistry, he could not find a textbook that met his needs and set out to write another one. Mendeleev’s initial approach was encyclopedic and already the first volume was over 500 pages long while addressing only 8 of 63 then know elements - carbon, hydrogen, oxygen, nitrogen the halogen elements (chlorine and its analogs). The second volume was to cover the remaining 51 – Li, Na, K, Rb, alkali metals, etc – and was under threat of becoming too big for students to read and comprehend. In search of providing a concise guiding principle, Mendeleev first discovered similarity in variation of properties of halogens and alkalis in the progression of atomic weights – i.e., the two groups of dissimilar elements - and he wondered if other groups of elements exhibited similar properties and soon established that the order of atomic weights could be used not only to arrange the elements within each group but also to arrange the groups themselves. Thus, in his effort to make sense of the extensive knowledge that already existed of the chemical and physical properties of the chemical elements and their compounds, Mendeleev discovered the periodic law: "…elements arranged according to the value of their atomic weights present a clear periodicity of properties."



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Fig.3: "Опыт системы элементов…/ Essai d'une système des éléments d'après leurs poids atomiques et fonctions chimiques par D. Mendeleeff, professeur de l'Université à Saint-Pétersbourg" - the first formulation of the Mendeleev's first periodic law of elements dated Feb. 17 (old style, Mar.1 – new style), 1869: (a- left) the handwritten manuscript as sent to publication and (b -right) the first published version in the 2nd print of the 1st edition of Mendeleev's "*Principles of Chemistry*".

There were many contradicting timelines of the discovery and its publications in the science history literature over the past century. Most widely accepted claim is that the discovery of the Periodic Law was published by Mendeleev on February 17 (old style, o.s., March 1, new style, n.s.), 1869 is not exactly correct. The most comprehensive critical study of all historical and bibliographical data and previously unknown archival documents and unaccounted historical records has been undertaken recently in Ref.[10] and established the chronological sequence of the discovery's publication which starts with the final manuscript of the *Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity* (Fig.3a) being submitted to publisher on February 17 (March 1), 1869, the very first publication of the Periodic Table was in the 2nd print of the 1st volume of the Principle of Chemistry (Fig.3b) on March 14/15 (26/27), 1869, shortly followed by printing of 150 one-pagers in Russian and 50 in French on March 17/20 (March 29/April 1) which were sent by Mendeleev to his many colleagues in Russia and Europe. Then followed the first publication abroad [Ref. 11], in German, dated April 5/7 (17/19) and the first appearance in Russian scientific periodical *Journal of Russian Chemical Society* in mid-May 1869 [Ref 12]. The first brief public communication of the Periodic Law was made by Mendeleev's colleague Nikolai Menshutkin at the meeting of the *Russian Chemical Society* on March 6 (18), 1869 [Ref 5].

The original form of the Table shown in Fig. 3 did consist of six columns each of 2 to 19 elements. To make it look like the modern periodic table we know one has to rotate it 90° clockwise, and flip left to right, that was soon done by Mendeleev himself in subsequent publications. Of course, the modern table has 118 elements versus 63 in the 1869 version and its modern day understanding – formed after the establishment of he quantum theory in 1920's – emphasizes periodicity of the properties of elements according to their number (i.e., number of electrons, rather than atomic weight). Naturally, the original table did not have the groups for lanthanoids and actinoids as well as for noble gases – all were introduced later – and had incorrect weights and/or placements of nine heavy metal elements, compared to current ones (Yt, Rh, Pt, Os, Hg, Au, Tl, Pb), due to incomplete knowledge of then time. What made a Mendeleev's system a distinct difference from earlier attempts of de Chancourtoiss (1862), Odling (1864), Meyer (1864), Newlands (1864), and Hincrichs (1867) are i) its completeness, as it included all 63 known elements without exclusions; and ii) its general assumption as a law of nature and, therefore, predictive power – so, Mendeleev took the liberty of changing the accepted atomic weights of some elements and foreseeing still undiscovered elements and their chemical and physical properties – see those marked as "?=45" (named by him as *eka-boron*, eka meaning one spot down in the table, or Scandium, discovered in 1879), "?=68" (*eka-aluminium* , or Gallium, 1875, atomic weight 69.7), "?=70" (*eka-silicon* , or Germanium, 1886, atomic weight 72.6), "?=180" (Hafnium, 1923) and *eka-manganese* (Technetium-99, unstable element, 1937). One can be referred to vast literature on the history of these discoveries, remarkable story of the gallium density being more accurately predicted by Mendeleev than Lecock de Bois Baudodran's initial experimental results, and how gradually the periodic law and table became the framework for a great part of chemical theory. (see, e.g., Ref. [13]). By the time Mendeleev died in 1907, he, William Ramsay (1852–1916), discoverer of inert gases, and Bohuslav Brauner (1855–1935) carried out two very notable refinements of the periodic table, such as addition of a zero group of elements for inert gases entered, and of a special group for rare earth elements.

Other Major Scientific Activities

One striking feature of Mendeleev's long career is the diversity of his activities. The range of his research can be gleaned from the table of contents of his *Complete Works* [Ref 14]: Vol. I: Ph.D. and Master thesis (3 articles, 348 pages); Vol. II: Periodic law (7, 518); Vol. III: The study of aqueous solutions by specific gravity (11, 467); Vol. IV: Solutions (13, 560); Vol. V: Fluids (16, 310); Vol. VI: Gases (17, 692); Vol. VII: Geophysics and hydrodynamics (25, 468); Vol. VIII: Organic chemistry (29, 664).; Vol. IX: Gunpowder (34, 313); Vol. X: Oil (36, 830); Vol. XI: Fuel (40, 584); Vol. XII: Metallurgy (42, 1094); Vols. XIII and XIV: Principles of Chemistry (105, 1792); Vol. XV: "Theoretical Knowledge" and notes (62, 646); Vol. XVI: Agriculture and processing of agricultural products (68, 480); Vol. XVII: Technology (70, 858); Vols. XVIII-XXI: Economics (318, 2514); Vol. XXII: Metrology (86, 366); Vol. XXIII: Public education and higher education (93, 385); Vol. XXIV: General topics (96, 462); Vol. XXV: Supplementary materials (98, 804).

Below we briefly present some (not all) of his most notable scientific accomplishments.

Chemistry. About a third of more than a thousand Mendeleev' articles, books and brochures are on the essentially all sections of chemistry - the theoretical foundations of chemistry, inorganic, organic, physical chemistry, all areas of chemical technology of those times from metallurgy and energy to agricultural chemistry, chemistry of bakery, cheese making, winemaking, etc. In 1891 Mendeleev invented *pyrocollodion*, a kind of smokeless powder based on nitrocellulose, free of drawbacks of existing French and English gun powders (chemical inhomogeneity, inability to be used in large caliber guns, limited storage time, etc). This work had been commissioned by the Russian Navy, however they have failed to organized its manufacturing due to bureaucratic mismanagement, so, during the 1st World War, Russians had to buy the same type of gunpower in vast amounts from United States.

Physics. Throughout his career Mendeleev conducted a broad research in the field of physical chemistry, mostly focused on understanding molecular interactions on gases and liquids via record-precision measurements of their basic properties such as density, thermal expansion, surface tension, etc. In 1860, while on internship in Heidelberg, he studied temperature dependence of surface tension coefficients of various liquids and carried out numerous experiments with capillaries. It was known that the so called capillary coefficient $a^2=hr$ (where r is radius of capillary and h is meniscus elevation within it) relates to the surface tension coefficient σ – an indicator of intermolecular interaction - as $a^2=2\sigma/(g\rho)$ where g is acceleration of gravity and ρ is liquid's density. Mendeleev discovered that above temperature – named by him as "*absolute boiling point*" – the surface tension becomes zero, cohesion and heat of vaporization become equal to zero and the liquid changes to vapor, irrespective of the pressure and volume. Inversely, below that point any gas in a container can be condensed to a liquid solely by the application of pressure. The phenomenon since then was widely used for liquification of gases such as air, oxygen, nitrogen, helium, etc. Eight years later, T. Andrews independently studied compressibility of carbon dioxide and determined that the temperature of 30.9 ºC is the lowest at which CO_2 still can be compressed to liquid by application of pressure (74 atm) and coined the term "*critical temperature*" – now used commonly, despite the deeper meaning of Mendeleev's "*absolute boiling point*" [Ref 15].

Less profound but of methodological value is what we now call *Clapeyron-Mendeleev equation*. In 1834 B. P. E. Clapeyron found a relation between the physical quantities defining the state of an ideal gas: the gas pressure P, the volume of the gas V, and the absolute temperature $PV = BT$, where the proportionality coefficient B depends on the mass of the gas. In 1874 Dmitrii Mendeleev re-formulated the equation of state of an ideal gas to the modern textbook form by using Avogadro's law (according to which gases contain the same number of molecules N at the same values of P, V, and T) , that is $PV = (M/\mu)RT$ or $PV = NkT$, where N is the number of gas particles and k is Boltzmann's constant.

Fig.4: Dmitrii Mendeleev in his office of the director of the Chief Bureau of Weights and Measures (1897).

Metrology. Despite his theoretical inclinations to search for deep foundational reasons of various phenomena, Mendeleev was skillful and innovative master of physics and chemistry lab experiments. He is known for inventions of a differential pressure barometer, a pycnometer - a device for measuring fluid density, for many improvements of pressure probes, one-arm weights, vacuum pumps for gases, instruments for determining the alcohol concentration (spiritometers), etc. In 1890, Mendeleev had to resign from his chair at the St.Petersburg University following his support of protesting students, and soon was appointed director of the Central Bureau of Weights and Measures (see Fig. 4). He took part in preparation of the law "On Measures and Weights" adopted in 1899, which introduced a new system of Russian basic units – pound for mass, *arshin*

for length, etc , and ratios were established between arshin and meter, pound and kilogram and laid the foundation for organizing an extensive state calibration network.
In 1898 he publishes a fundamental work in the field of metrology "Experimental study of the fluctuation of weights". To expand the knowledge of the magnitude and nature of gravity, he turned to studies with pendula and built one hanging in a 23 m high tower through 15 m deep well, all temperature stabilized. In 1898 he instigated state and church commission aiming to switch from outdated Julian calendar (at that time it differed from the Gregorian one by 13 days) but failed.

Economics. Since late 1880's Mendeleev was attracted as a consultant to Russian Cabinet of Ministers on broad spectrum of economics and technology issues. He was one of the most active preparers of the taxation and tariff reforms undertaken by the Government at that time. He published numerous articles and reports on economics (4 volumes in *Complete Works*, more than 2500 pages) and sometimes valued his fundamental *Tolkovii Tarif (Explicit Tariff, or Study on the Development of Russian Industry in Connection with its General Customs Tariff of 1891)* over his *Principles of Chemistry.* The former indeed offers a very impressive analysis of Russian economy, comparative study of the economic policies of several countries – most notably England – over several centuries, vast factual material and, most importantly, and main principles of economic instruments (such as taxes and tariffs) which can lead country to prosperity. Favoring enlightened modern autocracy, he considered bourgeois democracy a hypocritical cover for the power of capital and argued that in Russia the market must necessarily be combined with the active role of the state in the economy. Mendeleev considered the national economy as a complex in which agriculture, industry, transport, science, culture, education, the church, the armed forces, etc. are proportionally developed and harmoniously combined and called to overcoming the dominant unilateral approaches to economic development. He advised to process agricultural products locally, called not to export grain, but instead the cattle grown with that grain, not grapes, but wine, etc.

He opposed monopolies, enriched by price gouging, suppressing competition and inhibiting technological progress. At the same time, Mendeleev justified and proposed mainly economic methods of combating unjustified capitalist profits - through combined capital, state-owned monopolies and cooperative enterprises. He saw the ideal enterprise where the owner would be a participant in all its aspects, knew every employee, and all the workers would be interested in the results of the common work.

"Nothing is as Instructive as Delusions of a Genius"

Russian physicist and Nobel laureate Pyotr Kapitza once wrote that "Nothing is as instructive as delusions of a genius" [Ref 16]. Mendeleev offered several remarkable examples of such "delusions".

All his scientific life Mendeleev warned against excessive enthusiasm for atomism - "... Atoms do offer simplicity of conception, but give no confidence" (in the 1906 edition of the *Principles of Chemistry*) – and did not fully believe in the atomic theory. He strictly delimited the concepts of "element" and "simple body" and built precisely a system of chemical elements, and not of simple bodies. To him an element was the smallest materially homogeneous "weighty substance with the sum of its own properties" entering into particles (molecules) of bodies and he classified "elementary individuals", the nature of which was determined by their atomic weight. Such formulation of the problem allowed Mendeleev to create the Periodic system, but prevented him from foreseeing modularity in the atomic structure and accepting the discovery of radioactivity, electrons, and many major achievements of science of the late XIX - early XX centuries. He reproached the modern scientific thought for him because it "got entangled in ions and electrons".

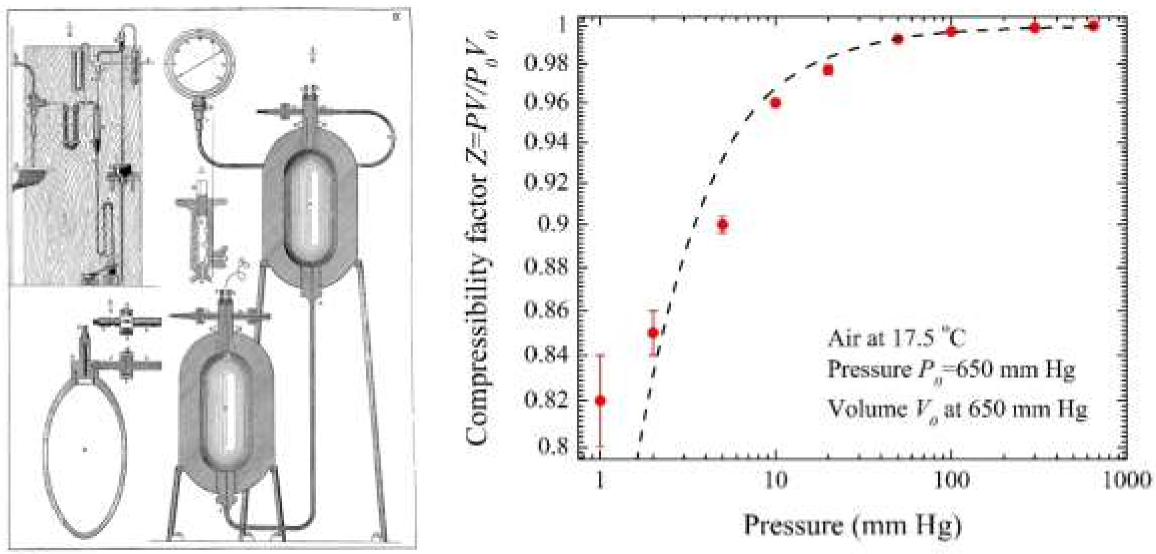


Fig.5: Mendeleev's experimental studies of rarified gases: (a - left) – laboratory equipment; (b – right) preliminary data on deviations from the Boyle-Mariotte law at low air pressure, red points – measurements in the range of 650 to 1 mm Hg [Ref. 18], dashed line – expected results under assumption of possible pressure underestimate of 0.3mm Hg.

Naturally, Mendeleev sought to understand the physical causes of the phenomenon of periodicity and believed that explaining the nature of periodicity "is possible only in the sense of a dynamic representation that can and must first of all explain the very concept of weight". Hence his interest in the question of "the cause of weight and attraction", as well as the properties of the medium transmitting light and gravity, i.e., luminous ether. He reasoned that existence of ether would manifest itself in additional term $f(P)$ to gas compressivity $PV = NkT(1+f(P))$ which grows at low pressures when the properties of an "ordinary" substance would cease to mask the properties of ether [Ref 17]. In his laboratory notebook of 1874 he wrote "Air has some density at zero pressure – and that is ether!". In 1874-75 he had undertaken search for so-called "positive deviations" from the Boyle-Mariotte law in highly rarefied gases (assuming $d(PV)/dP>0$) and seemingly observed them in several gases at pressures 650-100 mm Hg and below – see Fig.5. Such deviations were not subsequently confirmed and modern science does not know any deviations from the ideal gas compressivity except those at modest to high pressures which generally follow the van der Waals equation. Mendeleev's experimental setup for these studies was very sophisticated and expensive and relied on lavish support from the Imperial Russian Technical Society (RTO). As the results were hard to reproduce or explain without suspicion of an error in the pressure measurements (see

Fig. 5b), Mendeleev had published only detail description of the instruments and methods and other experimental results obtained at high pressures. Very quickly after the death of his chief laboratory assistant Mikhail Kirpichev in 1875, Mendeleev wrapped up and finished the program. He continued thinking about ether and its relation to the Periodic system and, e.g. in the 1905 brochure "An attempt at a chemical understanding of the world ether" the symbol *x* for ether was inserted in the Periodic table's zeroth group and zeroth raw, above the noble gases, with its weight estimated out of cosmological arguments to be between 9.6 10^{-7} to 5.3 10^{-11}. Neither that *element x*, nor another novelty of *element y* of the same group, so called *coronium* with mass 0.4 or less, could not hold their place in the Table. In line with the ether search and considerations, Mendeleev developed a theory of upper atmosphere and took a widely publicized balloon flight on August 7, 1887 in order to observe a solar eclipse – he rose to a height of 3800 m and flew some 100 km.

Mendeleev also studied petroleum origin and concluded hydrocarbons are abiogenic and form deep within the earth via reaction of water with iron carbide "The main fact to note is that petroleum was born in the depths of the earth, and it is only there that we must seek its origin in" [Ref 19]. The abiogenetic model was later further supported by many, including V.Vernadsky, but nowadays it is generally not well accepted by the scientific community which mostly stands by increasingly sophisticated biogenetic models of formation of hydrocarbon deposits in nature.

Mendeleev and Italy

Mendeleev's connections with Italy were very broad. He greatly appreciated foundational works of Amadeo Avogadro (1776-1856) and Stanislao Cannizzarro (1826-1910) the former for his for contribution to molecular theory (the Avogadro number), the latter for his influential role in the atomic-weight deliberations of the Karlsruhe Congress in 1860, which he often mentioned the Karlsruhe congress as the major event that led him to the discovery of the relations between atomic weights and chemical properties. He also adored Italy, its people and culture. He traveled there at least on six different occasions in 1860 (twice), 1864, 1879, 1881, and 1904 and visited Rome, Genoa, Bologna, Venice, Palermo, Catania, Naples, Aosta, Chiavenna, Menaggio, Porlezza, Ivrea, Arona, Como, Bellagio, Torino, Novara, Bergamo, Padova, Brescia, Verona, Milano, Pisa, Firenze , Civitavecchia, Albano, Anacapri, Castellammare, Sorrento, Messina, Canicatti, Caltanissetta, Agrigento, Bolzano among others – see Fig.6a. On November 12, 1860 Mendeleev saw Giuseppe Garibaldi in Naples and later reflect in his letter to family and friends *"…How proud must be the country should be which can produce people like Garibaldi !"*. His companion on that travel in the Fall of 1860 was Alexander Borodin (1833-1887) – his close friend, a fellow chemist student in Heidelberg (see Fig. 6b) and future professor of chemistry and internationally renowned composer of the "Prince Igor" opera and other jewels of world's musical culture. The beginning of Borodin's and Mendeleev's trip to South Italy was accompanied by a small curious incident, the story of which from the words of Mendeleev was written down by his chemistry student and future academician Vyacheslav Tishchenko (1861-1941) [Ref.20]: "In that year, the fight for freedom between Italy and Austria for the independence of Italy was still happening. On the Austrian border, near Verona, a rigorous check of those passing through was conducted. When it came time for Mendeleev and Borodin turn, they were detained and sent to a separate room. Why, for what purpose, we could not understand. I was left alone, but Borodin was ordered to fully strip.

Not sensing anything serious, A. P. [Borodin] got quickly undressed and even performed an entrechat in jest. He was thoroughly examined, and then we were released. We sat down in a train car. We had just crossed the border as Italians riding with us ran to us, shaking hands, thanking us for something, started treating us to wine. At first, we could not understand why. Turns out, that Borodin looked like an Italian politician after who the Austrians were vigilantly searching for. A. P. distracted them, and the Italian, riding in the same train car, safely escaped arrest." The name of the Italian revolutionary has not been solidly identified yet, though some suggest that could be either Nino Bixio (1821 – 1873) Garibaldi's lieutenant, one of the most prominent figures in the Italian unification - see Fig. 6c, or other younger (closer to Borodin's age) military commanders such as Giuseppe Missori (1829-1911) and Giovanni Chirassi (1832-1826) [Ref. 21].

Fig.6: (a - left) the 1860 rout of Mendeleev and Borodin in Italy; (b – middle) Alexander Porfierievich Borodin (1833-1887); (c – left) Nino Bixio (1821-1873).

Mendeleev's other trip to Italy in 1881 happened during his deep mid-life crisis. First, in November of 1880, despite being already a quite famous researcher in Russia and abroad, he was not elected to the St.Petersburg Academy of Sciences. The main reasons for that are thought to be fierce factional fights in relatively backward Academy, Mendeleev's rough character created him many enemies and the borderline nature of his periodic law on the junction of physics and chemistry (the academic opening was in the division of chemistry and technology). His almost two-decade long marriage to Feozva Lescheva (1828-1905) was also falling apart despite Mendeleev's immense love to his children – his son Vladimir (1865-1898) who later was a Navy officer and daughter Olga (1868-1950), future famous Soviet expert in thoroughbred hunting dogs. The 46 year old professor fell in passionate love with beautiful 20 year old art student Anna Popova (1860-1942). Attempts to stop the passion included a long fight for Feozva's agreement and church permission to divorce and Anna's escape to Rome but all in vain. At the end, Dmitrii Ivanovich got a break from teaching in the St.Petersburg university, permissions to divorce and to leave the country for Italy. In March 1881 he united with Anna in Rome and they had a honeymoon trip over to Napoli, Capri, and Florence followed by Paris and Spain. Mendeleevs returned to Russia in May 1881 and finally settled for church wedding in April next year (that was somewhat scandalous as their Orthodox priest agreed to wed them against the conditions of the divorce set by the Church authorities, which allowed Mendeleev to remarry only after some 7 years, being very handsomely bribed by the groom – and that led to the priest's eventual discharge from priesthood). The couple had four children - daughter Lubov' (the name for *love* in Russian, 1881-1939) – future actress and wife of one of the most famous Russian poets Alexander Blok (1880-1921), son Ivan (1883-1936), who became an experimental physicist and philosopher, and twins Maria (1886-1952), future director of Mendeleev's museum-archive in Leningrad/St.Petersburg and Vasily (1886-1922), a military engineer of tanks and airplanes. Seemingly no direct descendants of Mendeleev are alive nowadays.

Receipe for Genius : Breakthroughs, Recognitions and Myths

Mendeleev is among the most referenced names of Russian science, along with "father of Russian science", polymath and nature-philospher Mikhail Lomonosov (1711-1765) [Ref. 22], Nobel laureates Ivan Pavlov (1849-1936), pioneer in understanding physiological reflex mechanisms, and Lev Landau (1908-1968), a theoretical physicist, and biogeochemist Vladimir Vernadasky (1863-1943) – see quantitative analysis in Fig.1 of Ref. [Ref 23]. Among those Mendeleev is most closely compared as a personality and a scientist to Lomonosov: both were of humble roots and came from remote parts of North-East Russia, both got broad recognition in physical chemistry and had fierce temper, both were polymaths and tirelessly worked on educational initiatives, such as establishment of new universities in Moscow and Tomsk, correspondingly, and other matters of importance for Russia. Even some of their specific scientific interests were identical - they both worked on solutions, on the physics of liquids in capillaries, on the technology and physics of glasses, on economics problems and they both dreamed and planned expeditions to the Arctic. At the end of their lives, they both tried to better understand gravity and built large pendula for careful observations.

As noted above, Mendeleev was not elected to full membership of the St.Petersburg Academy, never sought that honour again and remained its corresponding member. Michael Gordin considers the non-election scandal as arguably one of the most influential events that propelled Mendeleev to true national-wide fame in Russia [Ref 6]. For several following years Russian advanced society, newspapers and journals commented on such obvious injustice, blaming foreigners (many voting Academy members, all Russian citizens, had German-like surnames) and effectively appealing to nationalistic senses. That and the broad spectrum of Mendeleev's involvements in Russian economic, scientific and state affairs made him extremely popular, and that popularity was further amplified during Soviet times, when Mendeleev was rightfully considered as "…the brilliant son of a great nation". Nowadays the scientist's namesakes include a city, lunar crater and volcano on one of Kuril islands, numerous streets and squares, Tyumen International airport, Russian Chemical Society, Moscow's Russian University of Chemical Technology and four other higher education institutes. More than two dozen Mendeleev monuments and bas-reliefs are erected in Russia, Ukraine, Azerbaijan. In 1962 the USSR (now – Russian) Academy of Sciences established D. I. Mendeleev Gold Medal for outstanding scientific work in the field of chemical science and technology.

List of Mendeleev scientific accolades catalogues memberships in 121 academies, institutions and societies including 50 foreign ones, such as an honorary doctor degree in the Accademia delle Scienze di Torino (1893), foreign membership in Accademia dei Lincei (1893) and Società Italiana di Scienze Naturali (1901), foreign corresponding membership in L'Accademia delle Scienze dell'Istituto di Bologna (1901) – see Fig.7 – and the 1882 Davy medal, the 1889 Faraday medal and the 1905 Copley medal from British learned societies [Ref. 5]. In 1905, Mendeleev was elected a member of the Royal Swedish Academy of Sciences and nominated for the Nobel Prize in Chemistry. While that year he did not get it due to confusion over how recent the recognized discovery should be (the periodic system was almost half a century old by that time), the following year the Nobel Committee for Chemistry did actually recommend to the Swedish Academy to award him the prize but suprizingly he did not get it. The details of that gross injustice can be found in Ulf Lagerkvist's book [Ref 24] and reveal intervention by Swedish chemist Svante Arrhenius, who had himself won the prize in 1903 for the theory of electrolytic dissociation, which Mendeleev had been an outspoken critic of for long time. Two additional nominations the following year were in vain as Mendeleev died of pneumonia on January 20, 1907.


Academia Scientiarum
Instituti Bononiensis.

Fig.7: Mendeleev's diploma of foreign corresponding membership in L'Accademia delle Scienze dell'Istituto di Bologna (1901) from collection of the D.I.Mendeleev Archive-Museum in St.Petersburg University.

Mendeleev championed involvement of women in science and experimental labs. After his death, one of his most talented lab assistants, Olga Ozarovaskaya, had become a famous folklorist and country's leading theater theorist and critic, and left very vivid memoirs on her assistantship years with Mendeleev [Ref 25]. Mendeleev tireless campaign against "mediumistic phenomena" and "spirits" received wide publicity in society and notably contributed to the establishment of the authority of science in the 19th century Russia as well as his lifelong commitment to writing numerous articles on popular science and technology for journals and encyclopaedias such as, e.g. for the Brockhaus Enzyklopädie and a series of publications entitled *Biblioteka promyshlennykh znaniy* ("Library of Industrial Knowledge").

Fig.8: "Mendeleev's Dream" monument opening on October 5, 2017 in St.Petersburg Murino district.

Characteristics for geniuses, Mendeleev's name is associated with wide-spread myths. One of them claims that the periodic table came to him while in sleep – see Fig. 8. The only documented evidence for that are memoirs of personal friend of Mendeleev, geologist and corresponding member of St.Petersburg Academy professor Alexander Inostrantsev (1843-1919). He wrote [Ref 26] "... Once, I, using the current placate mood of D.I. [Dmitrii Ivanovich], asked him a question, which pushed him towards his famous discovery. To this, he answered that he already suspected for a while the known bond of elements between themselves and that he thought long and hard on this. Throughout the last months before the discovery, Mendeleev used up a large amount of paper with the goal of finding a table form for his law, but nothing worked. Lately, he again began to work hard on this issue and, based on his story, was even close, but still, in the end, nothing worked. Just before the discovery of the law, Mendeleev had spent his time working on his elusive periodic table the entire night until morning, yet, nothing worked. Frustrated, he stopped working and, with a great longing for sleep, went, in his office, fully clothed, straight to sleep on the couch. In his dreams, he saw the clearly expressed periodic table, that later had been printed. Even in his sleep, his excitement was so great, that he instantly woke up and quickly sketched the periodic table on the first piece of paper he found lying on his desk. I bring up this story of Mendeleev because I see in it one of the best examples of the psychological impact of hard work on the brain of a person." There are two caveats though – firstly, Inostrantsev's manuscript was written after Mendeleev's death, and secondly, Mendeleev himself never communicated such a story and usually cited long and hard work toward the periodic system, with initial considerations of the problem traced to as early as decade and a half before the discovery - in his 1855 candidate (graduation from the State Pedagogical Institute) dissertation "Isomorphism in light of relation of crystal form to chemical composition" and his master's degree dissertation on specific volumes , which involved the study of the relations between various properties of chemical substances.

Fig.9: Illustrations to popular myth of Mendeleev being the father of Russian vodka – caricature by Vladimir Moltchanov and "Happy Birthday, Vodka!" greeting card from newspaper "Crimean Telegraph" No. 215 of January 18, 2013.

The myth of him being the inventor of Russian vodka – see Fig. 9a - is quite peculiar as Mendeleev himself did not drink vodka out of fear of becoming an alcoholic like one of his elder brothers and preferred red Georgian wine. Still, such a myth became wide-spread in the early part of the 20th century, when many in Russia wanted to add legitimacy to any possible piece of national culture. Other people, while accepting the fact that vodka existed several hundred years before Mendeleev, have perpetuated the legend that the famous chemist set the standard for vodka as a mix of 40% ethanol and 60% water. That myth has percolated through TV shows, literature, and even scholarly books, such as William Pokhlebkin's 1991 *History of Vodka*. It has also spread overseas along with the product and nowadays it is easy to find in liquor stores worldwide colorfully labeled bottles that proclaim, "In 1894, Dmitri Mendeleev, the greatest scientist in all Russia, received the decree to set the Imperial quality standard for Russian vodka and the 'Russian Standard' was born." Russian Standard is, of course, a brand of vodka, but the bottle's description makes the claim that there is something scientific about that standard as well. As an apex of this popular myth, January 31 – the day of the presentation and defense by Mendeleev his 1865 doctoral dissertation entitled

“A discourse on the compounds of alcohol and water” - is widely celebrated by many Russians as the “official vodka birthday” – see Fig.9b.

This myth, like vodka, has two parts truth and three parts water. Indeed, in his dissertation, Mendeleev sought to learn about the interaction of molecules by making precise $O(10^{-4})$ measurements of the density $\rho(C)$ and thermal expansion of a mix of ethanol and water at various concentrations C. His outstandingly careful and experimentally inventive and advanced measurements led him to conclude that solutions are the product of solutes and solvents combining into relatively stable chemical compounds. He argued that the points at which the second derivative $d^2\rho(C)/dC^2$ changes its value are indicative of stable molecular interactions. For example, for ethyl alcohol in water he found three such stable compounds as one molecule of spirit C_2H_5OH and three molecules of water H_2O at C=46.0% by weight or 53% by volume (corresponding to the mix volume contraction of about 2%); 1:12 at C=17.56% and 3:1 at C=88.46% - – see Fig 10a. Nowhere in his dissertation did he argue that vodka that is 40% alcohol by volume (C=34% by weight) is somehow optimal.

It is true that Mendeleev, as both a strong proponent of state-supported industrial development and a scientific expert on alcohol rectification, was part of a Russian government commission dedicated to introducing an efficient excise tax on alcohol and other consumer goods. By the early 1900s, the taxes he helped implement were bringing in about a quarter of the country’s revenue. But again, Mendeleev’s work with the commission was not about the best way to mix vodka.

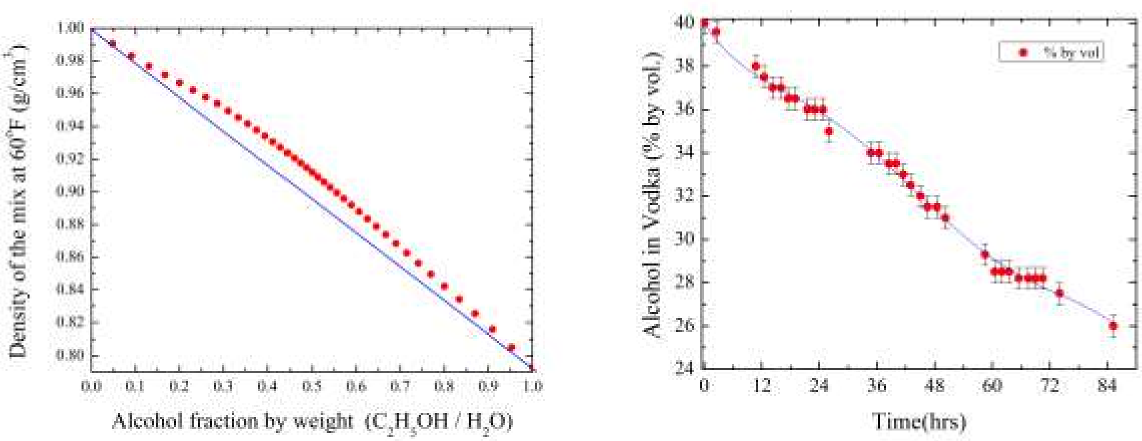


Fig.10: Physical properties of the ethyl alcohol solution in water: (a-left) in his 1865 doctoral dissertation “A discourse on the compounds of alcohol and water” Mendeleev meticulously studied physical properties of the solution, including the volume contraction phenomenon – red dots are the data, straight blue line indicates expectations in absence of molecular interactions; (b – right) a simple experiment with shot glass of vodka left untouched demonstrates that the alcohol and water in vodka do not evaporate at the same rate [Ref. 27].

Notably, the 40/60 or about mixture of alcohol and water shows several remarkable properties. At room temperature, the mixture is three times as viscous as either of its constituent components. And vodka out of the freezer is 2.5 times as viscous as it is at room temperature—that's why connoisseurs strongly advise drinking vodka very cold to fully enjoy its smoothness. In addition, a bottle of vodka left in a freezer won't burst: alcohol acts as an antifreeze, allowing the mixture to stay liquid down to approximately -25°C. Vodka is also potent enough that at room temperature its fumes can be set on fire - a phenomenon that has been used as a simple check of alcohol content since the 15th century to prevent barkeeps from watering vodka down. A similar standard for vodka instituted by Russia in the early 19th century required that no more than half the initial volume of liquid must remain after burning as reflected in its then common second name "polugar" (half-burned).

Another popular myth holds that you can pour vodka into an open glass at room temperature and enjoy it days later because the alcohol and water evaporate at the same rate. Vodka actually does not have such a property. After conducting simple home measurements with an optical spiritometer, we found that after about two days of standing at room temperature under normal conditions, the strength of vodka in a glass is reduced from 40% to 30% - – see Fig 10b [Ref 27].

To conclude, it is fair to say that Mendeleev's major discovery is among the topmost scientific breakthroughs which shaped our understanding of the Universe. Summing up and averaging various encyclopedia and history of science reviews, it is usually listed among "top ten" over the five centuries of modern science, such as: i) Copernican heliocentric system; ii) Galileo's nature-philosophy and telescope; iii) Newtons' gravity and infinitesimal calculus (with Leibnitz); iv) Lavoisier's principles of chemistry; v) Darwinian evolution; vi) Mendeleev's periodic system; vii) Einstein's relativity; viii) quantum mechanics and physics of Plank, Bohr and Heisenberg et al. ; ix) Watson and Crick's genetic coding mechanism; x) computers and internet. One can foresee further revolutionary advances this century, too - from artificial forms of life and conscience to teleportation and communication with extra-terrestrial intellect – but according to the Richard Gott's argument for longevity of observables [Ref. 28], it is safe to assume that Mendeleev's name will light up for at least another 150 years.

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Special Issue 6426, Science 363 (Feb. 1, 2019)

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