

ON THE BASIS OF THE PERIODIC ELEMENT SYSTEM

V. A. Etkin

Togliatti State University, Togliatti, Russian Federation
etkin.v@mail.ru

ABSTRACT

It is shown that the basis of the periodic system of elements is a cyclical change in the moment of distribution of valence electrons as one of the parameters of the inhomogeneity of the system. An approximate expression of this moment is found through the degree of filling of the outer shell of an atom and on its basis a graphical representation of a periodic law is proposed, taking into account its number, charge, atomic radius and distribution of valence electrons. The graph reveals the existence of additional periods ending in inert metals, not only in known elements but also in the group of lanthanides and actinides, allowing them to be organically incorporated into the periodic system. The consistency of such a representation of the classical and quantum models of atoms is shown.

Keywords: atom models, electron shells, oxidation state, chemical activity, periodic law.

INTRODUCTION

A century and a half have passed since D.I.Mendeleev reported on his system of chemical elements to the scientific community (1869) [1]. However, despite the long history of searching for a more perfect structure, the physical foundations of this system remain a great mystery to science. This is particularly true of the so-called short-period table of elements, which Mendeleev published two years after the discovery of the periodic law (1869) and which until the end of his life he considered the most perfect form of displaying the periodic law. He used it to predict the properties of undiscovered elements, it was she who was immortalized on the wall of the Mendeleev Memorial in St. Petersburg.

This "short" periodicity turned out to be perhaps the only major generalization in chemistry and physics, to which quantum mechanics of the twentieth century retreated, not finding an explanation. Indeed, according to quantum mechanics (QM), the shell filling scheme should obey the $2n^2$ rule (where n is the period number), i.e., represent the sequence of numbers 2, 8, 18, 32, 50, 72, 98. However, in the long-period filling scheme shells of this sequence is 2, 8, 8, 18, 18, 32, 32. The nature of such a systematic "doubling" of shells and periods of each new type after the first, two-electron shell (2-element period) is still not clear [2]. Since electronic or other structures that determine the existence of "short" periods do

not remain visible for decades, the very existence of "short" periodicity is currently being questioned. In particular, the International Union of Pure and Applied Chemistry (IUPAC) in 1989 officially recommended abandoning "short" periods. As a result, almost everywhere, except Russia and the CIS countries, preference is given to the long-period table. Assessing the situation as a whole, it can be stated that the periodic system of elements does not fit into the framework delineated by quantum mechanics [3,4].

At the time of establishing the periodic law (1869), there was no concept of the nucleus of an atom and an electron, the shell model of an atom, etc. No parameters were known that characterize the properties of various chemical elements [5]. Now there are already several parameters that periodically change with an increase in the charge number of atoms: the ionization energy of atoms; the energy of the affinity of atoms to the electron; electronegativity; atomic (and ionic) radii, etc. The dependences of these parameters on the atomic number of chemical elements are also constructed. However, the reason for the "short" periodicity has not been established. It causes a number of questions and a discontinuity of changes in the properties of elements, as a result of which atoms close in charge number appeared at different ends not only of short-period and long-period tables but also rows

constructed on the basis of the above parameters. Since true knowledge is knowledge of causes, and not effects, it is of interest to look "from the side". Such is the unified theory of nonequilibrium processes of energy transfer and transformation [6] according to which their common cause is the internal nonequilibrium (spatial inhomogeneity) of the system. The purpose of this article is to clarify the connection between the spatial inhomogeneity of the outer electron shell of the chemical elements of atoms with their position in the periodic system of elements.

Much closer to this goal is thermokinetics [10], which generalizes the TIP to continual systems that do useful work. From the standpoint of thermokinetics, the study of the

properties of spatially inhomogeneous (including structured) systems cannot be carried out without taking into account the spatial distribution of their extensive properties. In particular, the study of the properties of chemical properties of elements requires consideration of the distribution of electrons in the atoms of chemical elements. This inhomogeneity is characterized by the displacement Δr_i of the radius vector \mathbf{r}_i of the center of any material carrier Θ_i (mass M , entropy S , number of moles of the k th substance N_k charge Θ_e , components of impulse \mathbf{P} , its moment \mathbf{L} , etc.) from its equilibrium position. The position of their center is determined by the well-known expressions:

$$\mathbf{r}_i = \Theta_i^{-1} \int \rho_i \mathbf{r} dV; \quad \mathbf{r}_{io} = \Theta_i^{-1} \int \bar{\rho}_i \mathbf{r} dV, \quad (1)$$

where $\rho_i(\mathbf{r}, t) = \partial \Theta_i / \partial V$ is the energy carrier density as a function of spatial (Eulerian) coordinates \mathbf{r} and time t ; $\bar{\rho}_i(t)$ - its average value in terms of system V .

This immediately implies the emergence of a certain "moment of energy carrier distribution" $\mathbf{Z}_i = \Theta_i \Delta \mathbf{r}_i$. As applied to an atom, this moment acquires the meaning of an electric dipole \mathbf{Z}_e with a charge Θ_e and a shoulder $\Delta \mathbf{r}_e$. Naturally, the more completely filled the electron shells of an atom and the more evenly distributed the electrons in it, the smaller the dipole arm Δr and the moment of their distribution $\mathbf{Z}_e = \Theta_e \Delta \mathbf{r}_e$. For the inner shells of an atom completely filled, the arrangement of electrons in the shell is symmetrical, and the dipole arm $\Delta \mathbf{r}_e = 0$. Therefore, for neutral elements of the "noble" gases having a completely filled shell with the number of electrons n_{max} , the moment \mathbf{Z}_e is zero.

The situation is different when the outer shell is only partially occupied by valence electrons ($n_e < n_{max}$). In this case, the center of the electron cloud is displaced relative to the nucleus of the atom. In this case, the atom forms a "dynamic" (changing in magnitude and direction) electric dipole, the average value of which determines the dipole moment of the atom. As a consequence, the chemical activity of elements of the periodic system depends on the number of electrons in the outer shell of an atom. The elements that have the same number

of valence electrons in the outer shell belong to the same group of the periodic system. The asymmetry is reflected in the moments of the distribution of the valence electrons of \mathbf{Z}_e [11].

Thus, we come to the conclusion that one of the factors that determine the frequency of changes in the properties of chemical elements is the asymmetry of their outer electronic shells. According to the thermokinetic concept of equilibrium, spatially inhomogeneous systems (in this case, a set of valence electrons) being isolated, tend to an equilibrium, where $\mathbf{Z}_i = 0$ [12]. In the case of chemical elements, this means that the \mathbf{Z}_e moments tend to zero, which corresponds to the most stable electronic configuration with a complete external electron layer of n_{max} valence electrons. This number is in accordance with the classical "octet rule" G.N. Lewis (1916) is equal to 8. From the quantum-mechanical positions, the number of electrons in the outer orbit may be different, for example, equal to 18 or 32, that is, it does not correspond to the concept of valence. Therefore, the next task is to find the connection between the moment of distribution of electrons in the outer shell of the \mathbf{Z}_e atom and the degree of filling of the outer electron shell of the atom, which satisfies both the "octet rule" and the quantum mechanical model of the atom.

To do this, we take into account that for discrete systems, the moments of charge distribution \mathbf{Z}_e can be found using a simpler formula [11]:

$$\mathbf{Z}_e = \Theta_e \Delta \mathbf{R}_e = n_e e \Delta \mathbf{R}_e \quad (2)$$

where e is the charge of one electron; n_e is the number of electrons on the outer shell of an atom; $\Delta \mathbf{R}_e$ is the displacement of the center of the electron shell relative to the atomic nucleus.

Due to this anisotropy ($\Delta \mathbf{R}_e \neq 0$), an electrically neutral atom acquires the properties of an electric dipole with a charge $\Theta_e = n_e e$ and a shoulder $\Delta \mathbf{R}_e$. Since all atomic shells, except the outer one, are completely filled, only the outer shell affects $\Delta \mathbf{R}_e$, for which $\Delta \mathbf{R}_e = \mathbf{R}_e$ has the meaning of the atomic (covalent) radius of the chemical element. This takes into account the moment of the distribution \mathbf{Z}_e , which is dependent on the size of the atom. The German chemist U. Meyer (1870) discovered this dependence for the first time, challenging the priority of the discovery of the periodic law in

D.I. Mendeleev [2].

It is natural to assume that it is precisely the moment \mathbf{Z}_e that takes into account all these factors and characterizes to the greatest extent the chemical properties of atoms and their compounds. However, in view of the uncertainty of the distribution of electrons in the cloud (shell), in order to find \mathbf{Z}_e , it is necessary to resort to certain assumptions. To this end, we take into account that the atoms of elements with a completely filled outer shell ($n_e = n_{max}$) are symmetric so that the shoulder $\Delta \mathbf{R}_e$ of their dipole moment is zero, which determines their chemical neutrality. Therefore, in the first approximation, this shoulder can be considered a function of the degree of filling of the outer electron shell n_e/n_{max} :

$$\Delta R_e = R_e (1 - n_e/n_{max}) \quad (3)$$

Since the direction of the displacement vector $\Delta \mathbf{R}_e$ and the moment of electron distribution \mathbf{Z}_e does not play a role, the average moment of distribution of electrons of the outer shell (2) can be represented as:

$$\bar{z}_e = R_e e n_e (1 - n_e/n_{max}) \quad (4)$$

According to this expression, the moment of electron distribution vanishes twice: at $n_e = 0$, and at $n_e = n_{max}$, which determines the frequency of changes in the chemical properties of the element. At the same time, expression (4) remains valid for any number n_e and n_{max} , which makes the periodic law independent of classical or quantum models of filling the outer shells of an atom. In this case, you can build a

generalized graphical dependence of the moment of distribution of electrons for any element of the periodic system regardless of what we mean by n_e : the valence (oxidizing ability) of an element, its belonging to a certain group of elements of a short-period or long-period table, or the number of electrons on its external layer.

GRAPHIC REPRESENTATION OF THE PERIODIC LAW

As follows from expression (4), the inhomogeneity parameter for each chemical element is determined not only by the degree of filling of the outer shell n_e / n_{max} , but also by the size of the atom, depending in turn on the number of its electron shells (period number), and within the period - on the number of valence electrons on the outer shell (group numbers). This allows you to build a graphical dependence

in accordance with both the short-period and long-period table, relying only on data available in the literature [12] on the atomic (covalent) radii of the chemical elements of the periodic system and their maximum valence, without making exceptions for the elements of the lanthanides and actinides. The results of such calculations by expression (4) are shown in Figure 1.

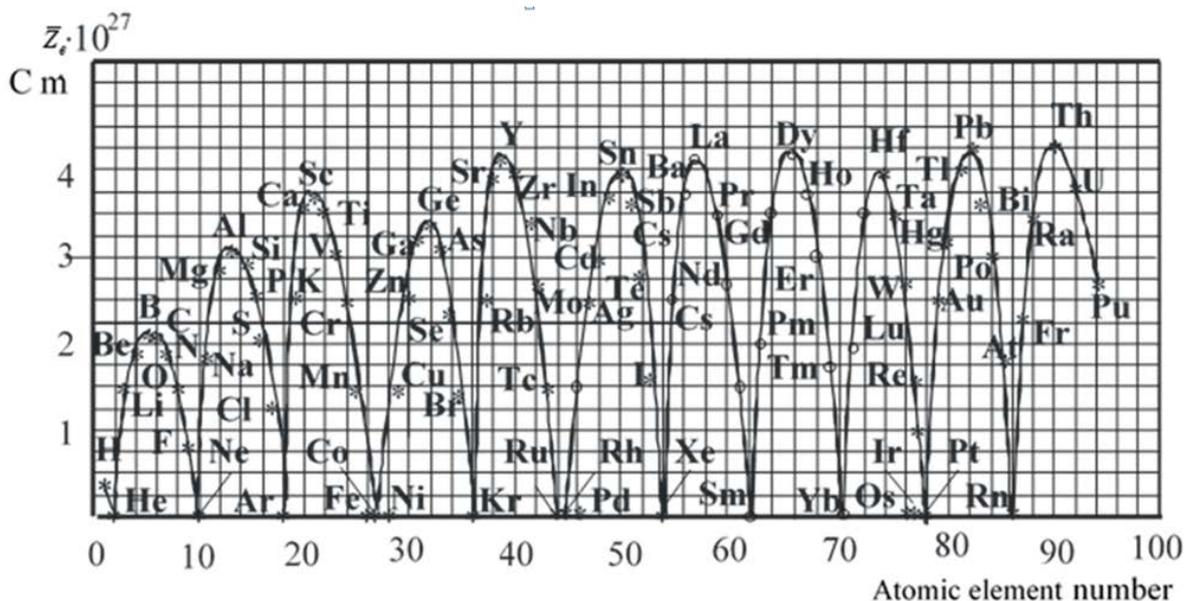


Figure 1. Graphic interpretation of the p[eriodic law. *- Calculated asymmetry of elements; ° - Predicted asymmetry of elemets

The first thing that catches the eye when looking at this graph is its continuous “sawtooth” character of changes in specific quantities without any discontinuities and jumps characteristically of such quantities as the ionization energy of atoms, the energy of the affinity of atoms to an electron; electronegativity as well as atomic (and ionic) radii [13]. This confirms the periodic law, according to the modern understanding of which “the properties of chemical elements and their compounds are periodically dependent on the structure of their outer shells”. At the same time, the graph in Figure 1 clearly shows that this

periodicity is due, on the one hand, to an increase in the number of electrons in the outer shell, which most easily interact with other atoms (that is, with an increase in the degree of filling of the outer shell n_e/n_{max}), and on the other hand, a decrease in its spatial asymmetry.

Another characteristic feature of the graphical dependence of Figure 1 is that the tangent of the angle of inclination of the tangent to any curve in Figure 1 characterizes the thermodynamic (relaxation) force, which tends to return the system to a uniform (internally balanced) state [10]:

$$\mathbf{X}_e = \partial U / \partial \mathbf{Z}_e, \quad (5)$$

This force changes its size and sign when moving from one element of the group to another. At the same time, according to Figure 1, the slope of the \bar{z}_e curve at the beginning of each period is maximum and decreases to zero as it approaches its maximum. The latter means that the strength of \mathbf{X}_e , which is a measure of chemical affinity, weakens by the middle of the period, and again reaches a maximum by the end of the period, but with a different sign. This corresponds to the experience according to which in each period there is a transition from active metals to less active, and then from low-active non-metals to very active non-metals. Moreover, at the end of each period (with the

transition to inert gases), this force abruptly vanishes, which explains the abrupt change in properties with the transition from the elements of the 7th group to the 8th.

The smooth increase in the specific moment of distribution from period to period is due to two opposing factors: on the one hand, the increase in the number of electron shells of the atom, and on the other hand, their compaction due to increased attraction to the nucleus. An equally smooth change in the strength of \mathbf{X}_e is also observed within each period.

The most characteristic feature of the graphical representation of a periodic law is that the parameter \bar{z}_e vanishes through a certain

number of atomic numbers Equal 8 ($n_{max} = 8$), which corresponds to the complete filling of the outer electron shell. This is due to a decrease in the moment of electron distribution by the end of the period and indicates the predominant effect of the symmetry of the distribution of electrons over their number in this layer. When the outer shell is completely filled, which is characteristic of such inert gases as He, Ne, Ar, Kr, Xe, and Rn, this is natural, since their valence is always zero. However, from the graph in Figure 1, it follows that this also applies to metals such as Co, Rh, Ru, Ir, Os, Rn, Pt, and Fe, for which chemical inertness is by no means characteristic¹⁾. For such elements, placing them in the same 8th group raises a number of questions. This indicates the need for further research with the doubling of certain periods.

Let the formation of outer shells occur in accordance with the quantum-mechanical model of the atom, that is, according to the $2n_e^2$ scheme. Then nickel Ni with atomic number 28 and shells 2,8,18 should fall into the category of elements with a completely filled outer shell $n_e = n_{max} = 18$, and $\bar{z}_e = 0$, i.e. at the end of the 3rd period, and not into the first subgroup 4th period. Similarly, palladium Pd with atomic number 46 (2,8,18,18), for which $n_e = n_{max} = 18$, and $\bar{z}_e = 0$ should go to the end of the 4th period, and not to the first row of the 5th period of the periodic table and especially not in the 2nd line of the long-period system. The same situation is typical for platinum Pt with atomic number 78 (2,8,18,32), which in this case also turns out to be $n_e = n_{max} = 32$, and $\bar{z}_e = 0$. The next inert element will be plutonium with atomic number 94 (2,8, 18,32, 18), in which $n_e = n_{max} = 18$, and $\bar{z}_e = 0$.

Thus, the presence in each period of the falling branch of the moment allows us to predict the possibility of the appearance of inert properties in nickel, palladium, platinum, and plutonium. You can also predict the appearance of the inert element of Nobelium No with atomic number 102 (2,8,18,32,18,32), for which $n_e = n_{max} = 32$, and $\bar{z}_e = 0$. However, in this case, the elements Fe, Co, Ru, Rh, Ir, Hf, and Mt fall on the descending branch of the corresponding

periods with $\bar{z}_e < 1$. In the eighth group, only the elements Ni, Pd, Pt and No will remain, for which $\bar{z}_e = 0$. This corresponds to their status as the elements most resistant to oxidation that brings them to the noble gases.

Such an approach is much more realistic than the existing assignment of the same 8th group to elements with equal and less than one. He leads to the conclusion that there are full-fledged periods, ending in inert metals so that there are significantly more of them than noble gases. At $n_{max} = 8$, they are short, as in the periodic table and in Figure 1. However, at $n_{max} = 18$ and 32, the periods stretch accordingly, so that the whole group of lanthanides and actinides fit well in them. Detection of inert properties of at least one element of these groups can serve as experimental confirmation of the presence of this periodicity and the erroneous placement of lanthanides (with an atomic number from 57 to 71) and actinides (with numbers 89-103) in the same cell 6- th and 7th periods [15]. A graphical representation of the periodic law eliminates this disadvantage.

The presence in Figure 1 of the falling branches in each row of the short-period table indicates the existence within the lanthanide group of two periodic subgroups with a similar alternation of their properties. Localized near Ba and Hf, they are clearly visible in the figure. This means that the lanthanoid group actually occupies not one cell of the table, but two (main and additional) series of the 6th period of the periodic table [10]. It is an equally clear indication of the existence of two subgroups of actinides with the numbers 89-103, following the radon. As a result, the number of periods in the periodic system described by graph 1 in the figure is slightly larger than the number of rows in the periodic table (for an additional period of lanthanides) and significantly larger than in the long-period table. Thus, the graphical representation of the periodic law explicitly indicates the possibility of continuing the table with the opening of additional, including inert elements. All these consequences of temokinetics do not contradict All these implications of temokinetics do not contradict quantum mechanics and predict the possibility of closing some periods of the periodic system not with inert gases, but with inert metals.

Graphic representation of the periodic law is more informative in relation to the tabular form. First of all, the graph in Figure 1 clearly shows

¹⁾ The exception is, perhaps, only the famous "Delhi column", which is not susceptible to corrosion for many centuries.

the difference in chemical properties between the closest elements of the same group. This difference in Z_e indicates possible variations in the configuration of the outer electron shell of an atom, depending on the location of electrons in it. It predetermines, apparently, the possibility of a change in the valence (oxidizing ability) of a given element due to the excitation of electrons of the underlying level.

Further, according to Figure 1, the position of the maximum serves as a smooth boundary for the transition from metals to nonmetals. Its position depends on many factors, the main of which is the degree of filling of the outer shell n_e / n_{max} with electrons. When $n_{max} = 8$, this position is close to the middle of the period, but it will shift to the right with increasing n_{max} . This corresponds to periodic tables on which the metal region shifts to the right. Therefore, the position of this maximum and the name of the corresponding transition This also applies to other factors affecting the value of \bar{z}_e max, in

particular, the radii of atoms. In particular, the "failure" of the maximum in the 4th period of the figure indicates the need to clarify the radius of germanium Ge.

This also applies to other factors affecting the value of \bar{z}_e max, in particular, the radii of atoms. In particular, the "failure" of the maximum in the 4th period of the figure indicates the need to clarify the radius of germanium Ge.

Summing up, we note that the main advantage of the research undertaken is the identification of the relationship between the chemical properties of elements and the heterogeneity parameter of the atom Z_e , which takes into account several factors, the inclusion of lanthanides and actinides in the periodic system, and the prediction of the existence of inert metals closing the periods along with the "noble" gases.

CONCLUSION

1. Consideration of the periodic law from the standpoint of thermokinetics as thermodynamics of heterogeneous systems allows you to enter a specific parameter of the heterogeneity of chemical elements, which characterizes the asymmetry of their outer electron shell.
2. This parameter, called the moment of distribution of valence electrons, takes into account the charge number of a chemical element, the number of its electron shells, the degree of filling of the outer shell and the radius of the atom, that is, it most fully reflects the structure of the chemical element and its position in the periodic system.
3. The moment of distribution of electrons undergoes cyclical changes in each period from zero to its maximum and again to zero, i.e. it has both an ascending and a descending branch with chemical elements located on them, thus excluding any jumps and gaps in their sequence.
4. The continuous sequence of chemical elements thus formed gives a new presentation of the periodic law, in which each period begins and ends with either inert gases or inert metals. This provision is essentially new and does not contradict either the classical or quantum-mechanical models of the structure of the atom.
5. A graphical representation of the periodic law allows us to include a group of lanthanides and actinides in a continuous chain, predicting the appearance of periods in them, similar to those previously known. As a result, the number of groups of elements covered by the periodic system exceeds that in the short-period and long-period system of elements.
6. The tangent of the slope of the curves when graphically representing the periodic law characterizes the strength of the interaction of the corresponding element with others and has in each period two maxima corresponding to the most pronounced manifestation of their reducing and oxidizing properties. The abrupt change in the sign of these forces during the transition from one period to another explains the abrupt transition to inert gases and does not violate the smooth increase in the number of shells of an atom with its age.
7. The proposed approach explains the origin of periodic repetitions of the properties of chemical elements by cyclically changing the degree of filling of external electron shells and eliminates the main difficulties in

constructing periodic tables, indicating the existence of additional short periods in the long-period system with an interval of 8 atomic numbers.

REFERENCES

1. D.I. Mendeleev. Periodic law (Main articles), M., 1958.(In Russian).
2. J .W. Spronsen. The periodic system of chemical elements. A history of the first hundred years, Amsterdam, 1969.
3. G.P. Gordeev. Three problems of the theory of the periodic system of chemical elements and their common solution. *Journal of General Chemistry*, 42 (1972); 46 (1976); 49 (1979). (In Russian).
4. B.M. Kedrov, D.H Trifonov, . On modern problems of the periodic system, M., 1974. (In Russian).
5. Collection of articles "One hundred years of the periodic law of chemical elements", M., 1969; 1971. (In Russian).
6. V.A. Etkin, Synthesis and new applications of theories of energy transfer and transformation: Diss. ... d-ra tech. sciences. M., MEI, 1998. - 213 p. (In Russian).
7. Yu.S. Cherkinsky. General thermodynamics. - M .: Polieks, 1992. (In Russian).
8. S.de Groot, P. Mazur, Non-Equilibrium Thermodynamics, Amsterdam, 1962.
9. R. Haase Thermodynamik der Irreversiblen Prozesse.– Darmstadt, 1963.
10. V. Etkin, Thermokinetics (Synthesis of Heat Engineering Theoretical Grounds), Haifa, 2010.
11. V.A. Etkin, To the bases of the periodic system of elements. // *Bulletin of the Haifa House of Scientists*, 2008.-T.XV.16-20.
12. V.A. Etkin, New Criteria of Evolution and Involution of the Isolated Systems. Intern. Journ. of Thermodynamics (IJOT) 2018, 21(2), 120-126, doi: 10.5541/ijot.341037
13. Periodic table of the elements. – VWR Scientific Products, 2000.
14. D.I. Mendeleev, The attempt of chemical understanding of the world ether. S-Pb., 1905. 5-40.
15. L.Pauling, The nature of the chemical bond and the structure of molecules and crystals. 3rd ed. - L.: Cornell Univ. press, 1960. 644 p.