

Periodic Systems of Molecules as Elements of Shchukarev's "Supermatrix", i.e. the Chemical Element Periodic System

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Generations of Soviet scientists contributed invaluable insights into molecular classification. Unfortunately, this research is little appreciated in much of the world. Among these workers S. A. Shchukarev was of great importance. His and his followers' legacy includes a host of graphical displays showing enthalpies of formation of gaseous molecules from free atoms ΔH_a and standard enthalpies of formation of substances ΔH_f° plotted on the atomic number of the central elements, on their oxidation states, their internuclear separations, and other variables for a wide range of molecules. These graphs serve as databases, from which data can be extracted, to moderate precision, visually. We discuss graphs for one very limited set, or "pleiade" (gas-phase oxides of nitrogen), and for three much broader sets, or subsystems (gas-phase fluorides of all main subgroup atoms and oxides of transition-metal atoms in gas-phase and in STP conditions). When dissolved in water, molecules lose their identities but periodicity is echoed in the acids and aquocations that are formed. We show, as an example in tabular form, that redox potentials of high-oxygen acids containing S, Se, and Te change concomitantly with ΔH_a and ΔH_f of their hexafluorides. We present graphical evidence that three properties for cations of groups 1–3 (in the short version of the periodic chart) behave similarly and share the periodicity of the elements. One of the properties is related to the ionization potential, which is shown in a tabular example to vary concomitantly with energy of hydration. It was the ultimate goal of S. A. Shchukarev that the transformation of any one graphical database into any other, having different molecules under different conditions, would be made mathematically.

1. INTRODUCTION

1.1. Periodic Systems of Molecules. Several different periodic charts and tables of diatomic molecules, each having advantages and limitations, are reviewed in refs 1 and 2. All of them are subsumed by the outer matrix product periodic system.^{3–5} This system is tested graphically by plotting quality tabulated data on the two atoms' atomic numbers Z_1 and Z_2 . The plot for molecules being formed from atoms Li through Ne (period 2) is very closely mimicked by the plots for species whose atoms come from other periods (R_1 and R_2), as seen in Figure 1. The similarity of the terrains is a demonstration of the periodicity of these molecules. It also allows for transforming the address of each molecule from (Z_1, Z_2) to (R_1, C_1, R_2, C_2) , where R_i is the period number of atom i in the chart of the elements and where C_i is its group number. The outer matrix product periodic system of diatomic molecules consists of the molecular symbols embedded in this four-dimensional space. Using these four independent variables, the tabulated data have been treated with least-squares⁶ and neural network methods,^{7,8} resulting in the capability to make forecasts for large numbers of molecules not in the original tables.⁹

Tabulated data for triatomic molecules have been plotted on functions of the three atomic group numbers, one plot

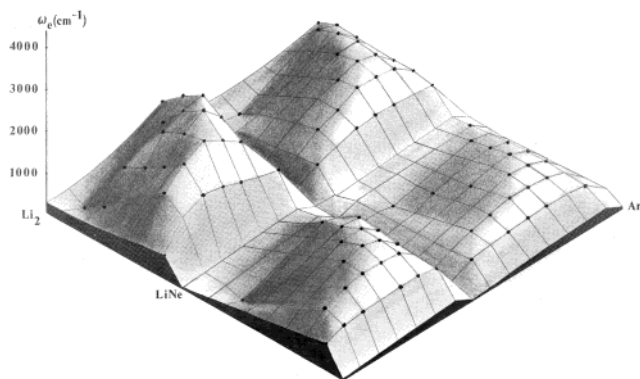


Figure 1. Vibration frequency vertically and Z_1 and Z_2 from 2 to 36 horizontally. Homonuclear molecules are on the left-right diagonal, and the terrain is symmetrical through a vertical plane on that diagonal. The similarity of the blocks demonstrates molecular periodicity. This figure is taken, by permission, from *Periodic Systems and their Relation to the Systematic Analysis of Molecular Data*; The Edwin Mellen Press: Winter Springs, FL, U.S.A., 1989.

for each choice of atomic *period* numbers. These plots demonstrate the periodicity of triatomics and lead to the outer matrix product periodic system of triatomic molecules, consisting of molecular symbols embedded in a space whose axes are R_1 , C_1 , R_2 , C_2 , R_3 , and C_3 . These plots allow the construction of functions which can be used to smooth the data and to forecast new data.^{8,10} These preliminary forecasts are comparable to preliminary neural-network predictions for the same molecules.⁸

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Periodic tables of polycyclic aromatic hydrocarbons,^{11,12} of functional groups,¹³ and even in principle of all molecules¹⁴ have also been created; they typically include molecules with various numbers of atoms. Unfortunately, few graphical displays of the data are provided.

It is significant that graphical displays such as Figure 1 serve to demonstrate periodicity and to facilitate least-squares fitting; it is not their role to present the tabulated data in a convenient form. For this reason it is of value to inspect the graphical “databases” of S. A. Shchukarev and his school, because they display the data so that their numerical values can be seen at a glance (to medium precision). There is another reason to survey his work: the strictures of the cold war resulted in a failure, on the part of much of the scientific community, to grasp the magnitude of the success that Soviet chemists achieved in the study of molecular periodicity. This study went far beyond classifications of isolated molecules to comprehend condensed-phase species and molecules in solution.

1.2. The Supermatrix Periodic System Enterprise.

Shchukarev considered the general periodic system as a supermatrix which binds together innumerable matrices pertaining to elemental atomic states, to ions, and to compounds that they may form; to their properties; to their functional dependences on the external conditions; and so on.¹⁵ Therefore the general periodic system, as he perceived it, includes the important possibility for quantitative conversion between the multitudes of matrices (or subsystems) embedded in the supermatrix—e.g., from those of all chemical element oxides (and their forms and properties) to those of all fluorides, hydrides, and so on.

The placement of a chemical element in the periodic table has vast symbolic significance. Its symbol is pregnant with an endless number of functions for the representations of its behaviors. “The system of the chemical elements represents a combination of points in an infinite (dimensional) space and is an object of special analysis using the assistance of operator calculus and group theory.”¹⁵

However, Shchukarev understood that it would be extremely difficult to make such purely mathematical conversions by the means available in his time. As an alternative, he chose to make a comparative study of the subsystems, showing specific regularities in forms and properties of chemical substances and exploring the possible construction of more general subsystems. The plan was that this analysis and its interpretation would lead to a deeper comprehension of the polyhedral periodic law, i.e., to the development of its theory. (His respect for the many aspects of the periodic law led him and his students to use various descriptors for it, such as polyhedral and polysemantic.)

In this article we will exhibit only fragments of Shchukarev’s research. These fragments were chosen to illustrate one of the ways to construct periodic systems of binary compounds and to see transformations of these on a change of the external environment of the molecules.

The starting points for Shchukarev’s study of compounds were problems unsolved since the time of Mendeleev: (1) What are the highest limiting forms of saturated compounds, or why do some elements not form the highest oxides allowed for them through the periodic law (e.g., ClF_7 and BrF_7)? (2) Why do some elements not form stable com-

pounds (oxides, halogenides, etc.), under usual conditions, with lower or some separate intermediate oxidation steps?

In the process of his investigations, Shchukarev reached conclusions about the questions concerning oxides as well as the analogous questions about the composition of pleiades of other compounds such as halogenides, chalcogenides, etc. (“Pleiades” was Shchukarev’s favorite term for qualitative sets or groups.) It is necessary to consider not only the number of electrons in the outer shell of the central atom (given by its group number in periodic system of the elements) but also “the chemical nature of the second element-partner, the enthalpy of formation of the molecules from free atoms, the ionization potentials of both partners, as well as the condensation energies of the obtained compound”.¹⁶ For the solution of the problem concerning the stability of any compound, one must study the competition between all conceivable compounds in a pleiade, taking into account the enthalpy and the entropy, and thus including the influence of temperature.

In accordance with this credo, Shchukarev carried out a comparative analysis of the energies of formation for different states for the initial elements and for the products of their interaction. As a key to construction of the periodic system of isolated gaseous molecules, Shchukarev used the experimentally established fact that a joining of successive single atoms of a given element to a chosen central atom is accompanied by a discharge of energy whose quantity is gradually decreased as the coordination step n (the number of atoms, i.e., ligands, joined to the central atom) increases. Consequently, the dependence on n of the enthalpy of formation, $\Delta H_a(n)$, of gaseous compounds formed from free atoms in pleiades of molecules are approximately smooth lines with positive curvature (for the most part). These lines are suitable for the interpolation and sometimes for the extrapolation to ΔH_a of unstudied molecules. At the present time, ΔH_a values may be found in refs 17–19.

The extent of the curvature of the line $\Delta H_a(n)$ is dependent on the enthalpy of the mutual repulsion of the ligands, named by Shchukarev as the “coordination endoeffect”.²⁰ The presence of such an effect indicates that there will be some limit to the saturation of the central atom with ligands. The knowledge of the magnitude of the effect makes it possible to calculate theoretically the saturation limit, showing that it will take place earlier for larger ligand atoms and for smaller central atoms (other things being equal).

If in any pleiade there are molecules with even and odd numbers of valence-shell electrons, then the curve $\Delta H_a(n)$ for the even-electron molecules is found to be lower than the curve for the odd-electron molecules, but sufficiently close to it so that interpolation is practically possible in this case as well.

Figure 2 illustrates the phenomena of curvature and of parity for nitrogen oxides.²¹ The same phenomena are seen in systems of more complex molecules, for example, of hydrocarbon molecules,²² of molecules of consisting of carbon, oxygen, and hydrogen,²³ and so on. Such figures serve as “databanks”.

Having such databanks for substances of each element, it is possible to construct a great number of periodic subsystems (matrices) for molecules of different types. Four examples of such subsystems will be presented: one contains gaseous fluorides of the principal subgroup elements of the periodic

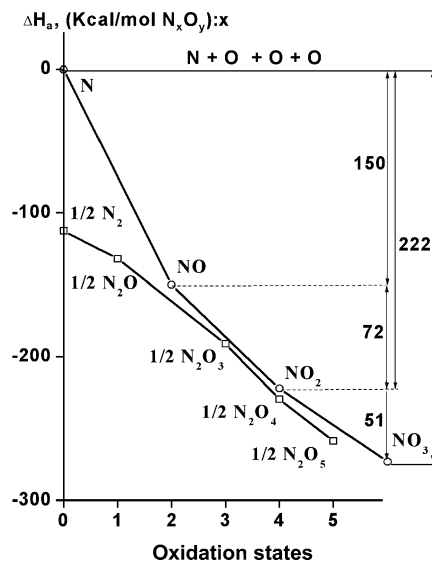


Figure 2. ΔH_a for gaseous oxides of nitrogen as a function of oxidation state. The species on the lower line have an even number of electrons.

system (*s* and *p* elements); two others contain gaseous and STP oxides of the complementary subgroup elements (*d* elements); and the last contains molecular fragments in the aqueous environment.

2. GASEOUS MAIN SUBGROUP ELEMENT FLUORIDES

The first example of a subsystem is shown in Figure 3.²⁴ It shows how ΔH_a depends on the ordinal number of the

core element *Z*. This web of molecular states represents the subsystem for gaseous fluorides of the main subgroup elements. In this figure, various types of compounds are connected differently in order to show the regularities that they have:

- Fluorides of any selected element (no lines, but seen on verticals).

- Isoformular octet fluorides such as LiF, NaF, KF, ..., OF₂, SF₂, SeF₂, ... and CF₄, SiF₄, GeF₄, ..., where the central atom changes periods and the number of fluorines is constant (dashed lines connecting pleiades).

- Isoformular fluorides such as NaF, MgF, AlF, ... where the central atom changes position along a period (thin lines), and such as PF₅, SF₅, ClF₅, ... where the central atom also changes position along the second halves of periods (dotted lines).

- Fluorides completely saturated with fluorine by means of *s* and *p* valence electrons, without making use of extra-valent *d* electron vacancies, including LiF, BeF₂, ... OF₂, F₂; ... NaF, MgF₂, AlF₃, ... ClF and so on (thick line).

The absent transition-metal elements are indicated when the thin and thick lines have a dashed segment.

It is seen that for many elements in Figure 3 there are compounds at all coordination numbers without exception, from the first to the maximum which is allowed by the periodic law, that is, which corresponds to the group number (notice BF, BF₂, and BF₃, and PF through PF₅). It is seen that no element possesses a fluoride coordination larger than its group number. Obviously the upper limit of ligand number

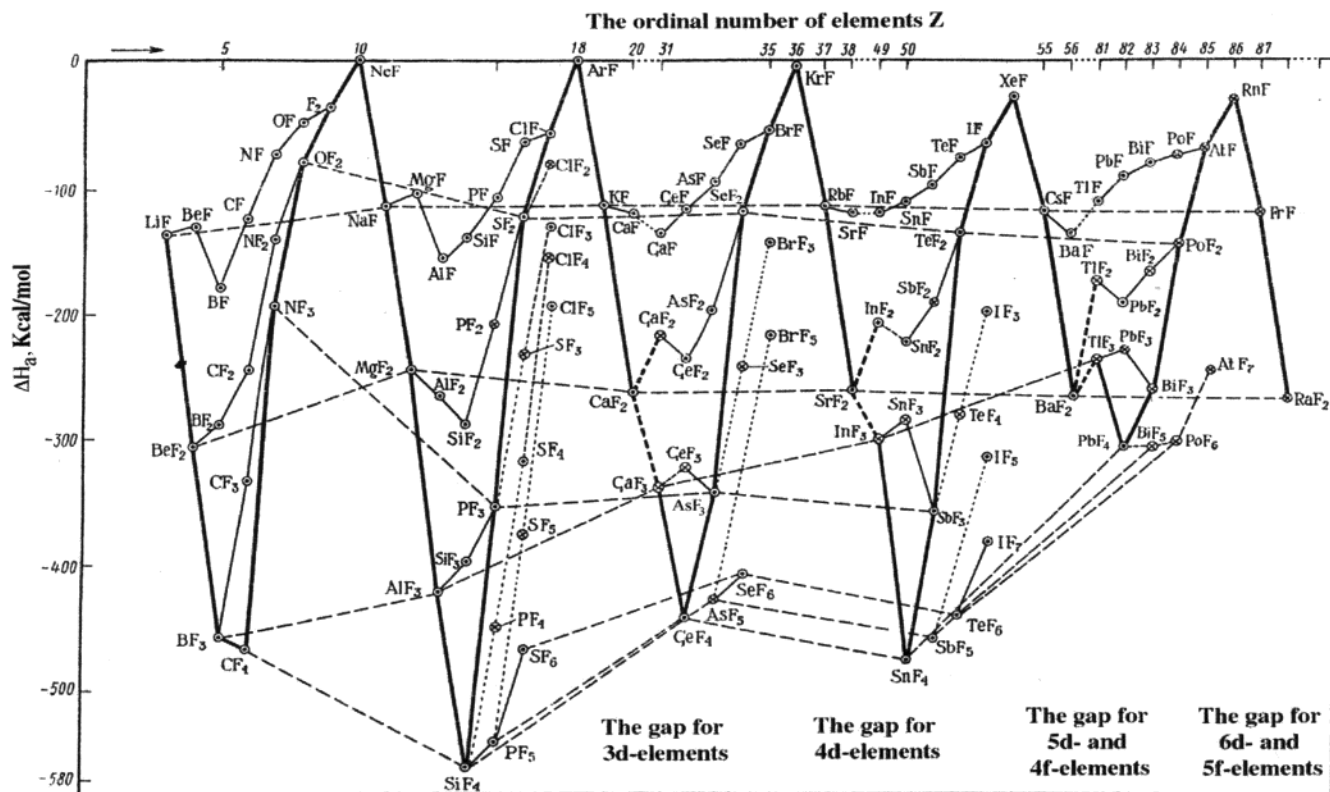


Figure 3. Enthalpies of formation from free atoms for gaseous fluorides of main subgroup elements plotted against atomic number *Z* (but with gaps for *d* and *f* elements). Some of the values of ΔH_a , marked with crossed circles, are the results of interpolation or extrapolation; these are usually unstable forms of fluorides with intermediate coordination states, such as PF₂, PF₄, SF₃, SF₅, ClF₂, ClF₄, and so on. The cause of their instability is obviously in that the molecules are odd. Thanks to their situation on the curve $\Delta H_a(n)$, above the curve for even molecules, they can dimerize themselves by bonding their unpaired electrons or can disproportionate into two neighboring even molecules (for example $2PF_4 \rightarrow PF_3 + PF_5$).

is determined by the electronic shell structure of the central atom.

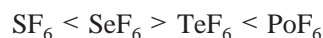
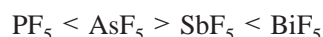
However the highest observed coordination state is not always the maximum allowed. For instance, fluorides with high coordination states are absent not only for nitrogen and oxygen but also for chlorine and bromine (the absence of ClF_6 and ClF_7 in the chlorine pleiade and of BrF_6 and BrF_7 in the bromine pleiade). The former pleiades (of nitrogen and oxygen fluorides) can be justified by the absence of energetically advantageous extravalent vacancies in the electronic shells of the core atom. The latter pleiades (of chlorine and bromine fluorides) can be understood as due to the coordination endoeffect. By contrast, the atom iodine, which is bigger than the chlorine and bromine atoms, has a smaller endoeffect of coordination; accordingly, the highest fluoride IF_7 is stable. In this way, the questions formulated in the fifth paragraph of section 1.2 have partial answers.

As for energetics, the characteristic features of the system are as follows:

- The strongly pronounced periodicity of the thick continuous line, uniting the saturated fluorides of the second-period elements and analogous fluorides in the rest of the system. The form of this periodicity is explained mainly by an increase in the number of fluorine atoms from the beginning of the period to the element of the fourth group (C, Si, Ge, Sn, Pb) and by a decrease in their number toward the end of the period.

- The less obvious but more diversified periodicity of isoformular lines for diatomic molecules (not all pleiades of which are connected with lines). These result from the superposition of increased numbers of bonding, and then antibonding, electrons in periods; the valence-state excitation energies of beryllium and magnesium; the presence or absence of extravalent electronic vacancies in atoms; and so on.

- The nonmonotonic way in which ΔH_a varies in subgroups such as



This phenomenon is called secondary periodicity.

3. SECONDARY PERIODICITY

Secondary periodicity is explained^{25,26} by the fact that in each even period, electrons for the first time fill up the orbitals with a new azimuthal quantum number. In the second period it is the p orbitals; in the fourth period, the d orbitals; and in the sixth period, the f orbitals. The screening by inner-shell electrons has the result that the inner part of the valence-electron orbitals are very close to the atomic nucleus; this makes removing valence electrons or changing them to a different orbital very difficult. The s electrons are mostly influenced by screening, and that is why secondary periodicity is mostly evident at the highest oxidation states of the elements.²⁵

The filling up of new symmetry orbitals with electrons (Shchuckarev called such orbitals "kainosymmetric," from the Greek $\chi\alpha\acute{\iota}\nu\omicron\varsigma$, or new) accounts for more than the

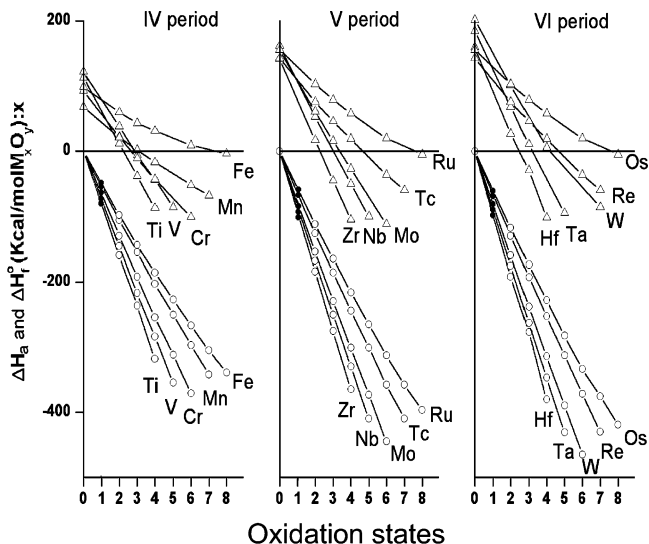


Figure 4. The enthalpy of formation for gaseous oxides plotted on the oxidation state for group numbers 4–8 of the chart of the elements. The points can be related to unit steps on the abscissas as follows: 0, M; 1, $(1/2)\text{M}_2\text{O}$; 2, MO ; 3, $(1/2)\text{M}_2\text{O}_3$; 4, MO_2 ; 5, $(1/2)\text{M}_2\text{O}_5$; 6, MO_3 ; etc. The clear circles represent experimental values, and the black ones represent interpolations. The lower data pertain to molecules produced from free gaseous atoms, and hence the ordinate is ΔH_a ; the upper data relate to molecules produced from solid metals and molecular oxygen, and hence the ordinate is ΔH_f° .

phenomenon of secondary periodicity, which is clearly expressed in the properties of elements with filled kainosymmetric shells. It also influences the properties of kainosymmetric elements themselves, where the filling in of kainosymmetric orbitals is still taking place (H and He are $1s$, B through Ne (period 2) are $2p$, Sc through Zn (period 4) are $3d$, and Ce through Lu (period 6) are $4f$ kainosymmetric atoms). These elements have anomalously high ionization potentials and small sizes. For the $2p$ kainosymmetric elements it leads to the fact that the variation of ΔH_a for monofluorides proves large in comparison with those for $3p$, $4p$, and $5p$ elements (Figure 3). It occurs because of the increased effects of accumulating bonding (at the beginning of the period) and antibonding (at the end) electrons in the narrow internuclear space in molecules.²⁷

4. THE PERIODIC SUBSYSTEM OF OXIDES OF COMPLEMENTARY SUBGROUP ELEMENTS (TRANSITION METALS) AND ITS TRANSFORMATION AT STP

The transition from the subsystem of fluoride molecules to those of other compounds is accompanied by quantitative and qualitative changes. For example, the pleiade of gaseous hydrides is totally different than that for gaseous fluorides.²⁷ For all systems of gaseous compounds of main subgroup elements with oxidizing elements (other halogens, oxygen, and other chalcogens) the same regularities must in general take place.

As to the transition-metal elements, the system of gaseous binary compounds with oxidizing elements has both similar and specific features compared to the subsystems for main subgroup elements. The bottom curves in Figure 4 show the dependences of ΔH_a for gaseous oxides of the $3d$ -, $4d$ -, and $5d$ -metals of the first six d -metal subgroups.¹⁶ It is seen,

just as in the subsystem for the fluorides of nontransitional elements, that

- The lengths of the pleiades for all elements do not exceed the lengths permitted by the periodic law: the maximum oxidation state is equal to the number of the periodic system group. Besides, the coordination endoeffect is comparatively not large: the curvature of the lines is small. Therefore the electronic structure, and not the coordination endoeffect, defines the length of each pleiade.

- In each series of *d*-metals, the ΔH_a of the highest oxides are at a minimum where exists the maximum difference between the numbers of bonding and of antibonding electrons, i.e., with oxides of elements of group 6 (CrO_3 , MoO_3 , and WO_3).

Contrary to most of the cases in the subsystem of *p*-element fluorides (section 2), in the oxide subsystem of the *d*-metals ΔH_a for every group of metals becomes more negative with a growth of period number. Especially is this so at the transition from 3*d*-metal (kainosym-metric) oxides to 4*d*-metal oxides.

Since the oxides are present in all oxidation states of the central atom, the questions posed earlier do not relate to Figure 4. But it is necessary to remember that this and similar plots contain species that can exist only under "refined" conditions, i.e., under vacuum, when they are isolated and cannot come into contact and interact with one another.

But if the pressure is made higher, the picture is strongly changed. The previously isolated monomer molecules and atoms start to interact, forming dimers or polymers or being condensed or disproportionated. As a result, new extra components will enter the formation energy. There are great expenditures of energy on the atomization of the solid metals and molecular oxygen, and some energy is released when monomeric molecules are dimerized, polymerized, disproportionated, or condensed. This situation will be examined in detail.

For the upper group of lines in Figure 4 it was assumed that the gaseous oxides are formed not from free atoms of metal and oxygen but from the substances in their standard states (i.e. from solid metals and molecular oxygen). The result is that many of the gaseous oxides are formed endothermically, i.e., they are not stable compared to simple substances. Only the oxides at the end of the pleiades remain stable (upper part of Figure 4). The upper part of Figure 5 shows the same curves. But if not only the oxygen and metal atoms but also the oxides are allowed to assume their standard state phases, then, as a result of the energy discharge of oxide condensation, many of them again become thermodynamically stable, as shown in the lower portion of Figure 5.¹⁶

This occurs especially for oxides in the middle of pleiades, as they possess greater condensation energy than the oxides at the beginning and at the end of pleiades (shown by the vertical dashed lines in Figure 5), while some higher and lower oxides may be unstable. The higher oxides in some pleiades lose their stability because of the competition with the less saturated oxides. They exothermically evolve molecular oxygen to give a stable interstitial oxide (reaction 1). Some lower oxides disproportionate, i.e., turn into a stable

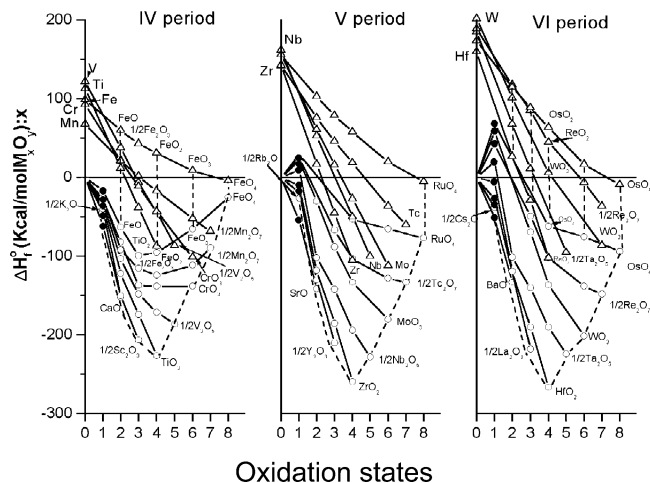
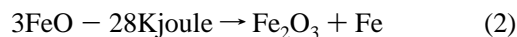
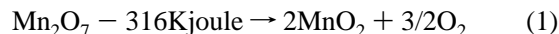


Figure 5. The upper portion is the same as the upper portion of Figure 4. In the lower portion ΔH_f^0 describes the situation where not only the elements but also their compounds are at STP. The dashed bag-shaped lines at the lower part of the figure connect the points for saturated oxides of different group metals. The similarities of the curves in the three parts of this and the previous figures is a manifestation of periodicity in the gaseous and condensed-matter phases.

oxide in a higher oxidation state and solid metal (reaction 2).



These and similar transformations bring us to a *tabular* form of the subsystem for *d*-metal oxides under standard conditions (Figure 6).

All of these data allow us to give the following answer to the above-mentioned questions. The reason for the absence of the compounds of some forms, allowed by the periodic law, consists mostly in the thermodynamic competition of compounds between themselves and simple substances, and it is connected in a very complicated way with the structure of these substances.

Despite these changes, the result of molecular condensation is that some of the regularities which pertain to the subsystem of gaseous oxides are still present under standard conditions. For example, for oxides in oxidation states 4 or more of the metal, the succession of standard formation enthalpies ΔH_f^0 is $3d \gg 4d > 5d$.

Subsystems of other compounds probably suffer the same changes in transition from vacuum to standard conditions but with their own peculiarities. As an example, see ref 20 on transition metal halogenides.

5. THE TRANSFORMATION OF MOLECULAR PERIODIC SUBSYSTEMS WHEN TRANSITIONING TO AQUEOUS SOLUTIONS

Large cardinal changes in binary compounds, and in the subsystems representing them, occur when the compounds dissolve in water. As a rule the compounds lose their completeness. They either dissociate into separate hydrated ions (e.g., reaction 3) or react with water either hydrolytically

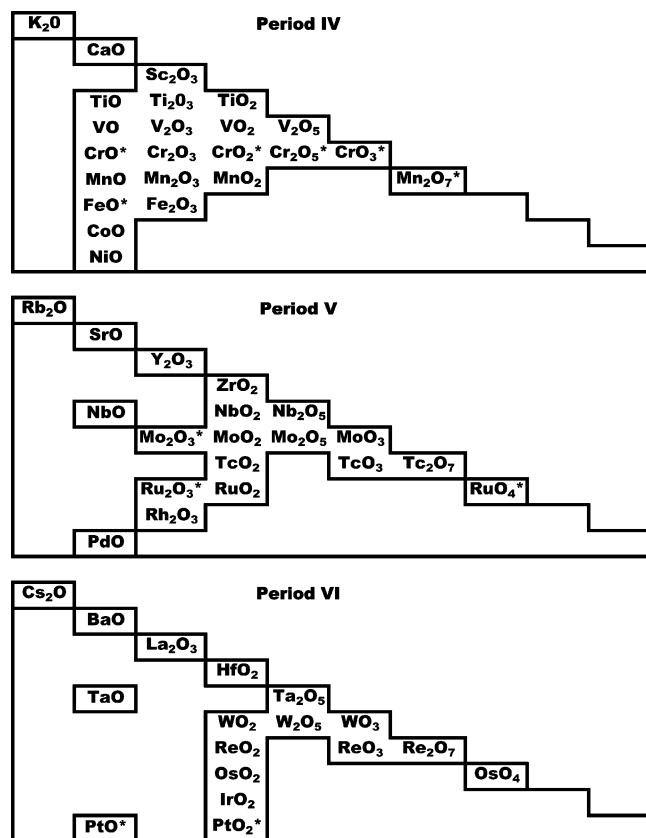


Figure 6. The system of d -metal oxides which are stable or metastable in standard conditions, in the form of a table. The oxidation state is the abscissa and the group number is the ordinate, for each of the three periods. Metastable oxides are marked with an asterisk.

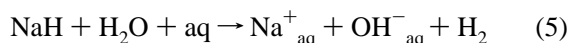
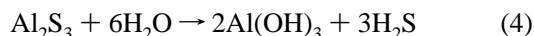
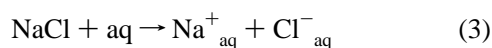
Table 1. Oxidation Abilities of Acids Compared with the Gaseous Compound Formation Enthalpy, ΔH_g , and with the Standard Formation Enthalpy of the Compounds in Their Standard States, ΔH_f°

		SF ₆		SeF ₆		TeF ₆
gas phase	ΔH_a , kcal/mol[18]	-711	<	-674	>	-720
		SF ₆		SeF ₆		TeF ₆
STP	ΔH_f° kcal/mol[18]	-292	<	-267	>	-315
		H ₂ SO ₄		H ₂ SeO ₄		H ₆ TeO ₆
aqueous	E_{VIV} , V[28]	0.17	<	1.15	>	1.02

Table 2. Formation Enthalpies of Gaseous Metal Fluorides, ΔH_a , Hydration Enthalpies of Metal Cations, ΔH_h , and the Sum of the First and Second Ionization Energies of Metals, ΣIP

	ZnF ₂ (gas)		CdF ₂ (gas)		HgF ₂ (gas)
$-\Delta H_a$, kcal/mol[27]	187	<	227	>	122
	Zn ²⁺		Cd ²⁺		Hg ²⁺
$-\Delta H_h$, kcal/mol[30]	493	>	436	<	442
	Zn		Cd		Hg
ΣIP , kcal/mol[30]	628	>	595	<	670

(reaction 4) or by oxidation–reduction (reaction 5).



As a result, dissolution of a whole system of binary molecules (fluorides, oxides, hydrides, and so on) leads to a number of subsystems: aquoions, hydroxides, acids, and

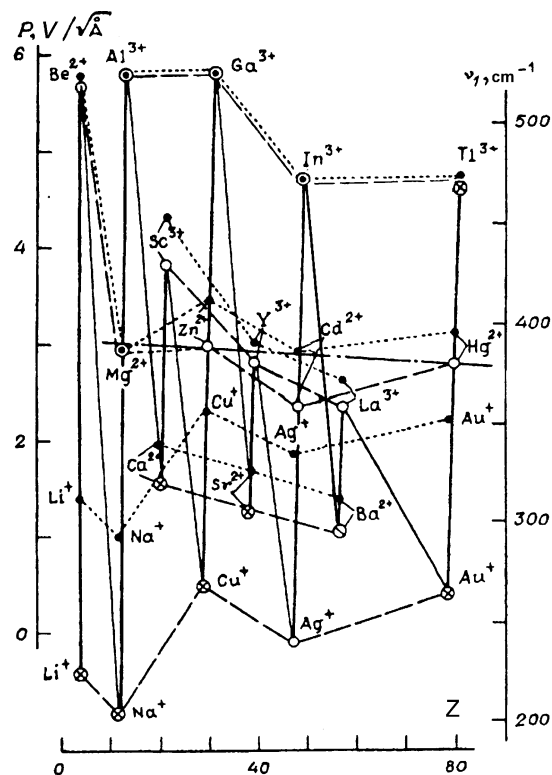


Figure 7. The periodic change of P for free cations (bullets) and of ν_1 for aquo-cations (open circles for experimental data, crossed circles for interpolated data) with the increase of element ordinal number Z . This figure has been reproduced as Figure 7a–d, Supporting Information, showing the following features separately. The thick upward-rising lines unite isoelectronic ions of the same period; the thinner downward-falling lines unite ions of the subsequent periods. The dashed and dotted lines connect ν_1 and P for metal cations of distinct periodic chart subgroups. For cations of the alkali-earth subgroup (Ca^{2+} , Sr^{2+} , and Ba^{2+}) and for the ions of the scandium subgroup (Sc^{3+} , Y^{3+} , and La^{3+}) isoelectronic to them, both properties change monotonically, diminishing with the growth of Z . For the subgroups which connect cations of the second and third *periods* and of complementary subgroups (Li^+ , Na^+ , Cu^+ , Ag^+ , and Au^+ ; Be^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} ; Al^{3+} , Ga^{3+} , In^{3+} , and Tl^{3+}) both properties change consistently with secondary periodicity. The relationships between these species is very clear in the short version of the periodic chart.

sometimes complex compounds which are formed between separate ions. Some of the subsystems seem to be “echoes” of the gaseous-compound subsystems; one can see in them regularities akin to those taking place in the subsystems of gaseous compounds. So there is a concomitance between the changes of ΔH_a for gaseous and of ΔH_f° for condensed, binary compounds and the oxidation ability of high oxygen acids, which are the products of oxides with water (e.g., reaction 6) or of the hydrolysis of halides (reaction 7):



For example such concomitance takes place for acids H_2XO_4 , where X is S, Se, or Te. It is seen in Table 1, where the oxidation ability of these acids is characterized by the standard reduction potential ratio $E^\circ_{\text{VI/IV}}$ for the system $\text{H}_2\text{XO}_4 + 2\text{H}^+ + 2e \rightarrow \text{H}_2\text{XO}_3 + \text{H}_2\text{O}$.

For the aquocations, the same concomitant relation to the stability of corresponding gaseous oxides, halides, and so

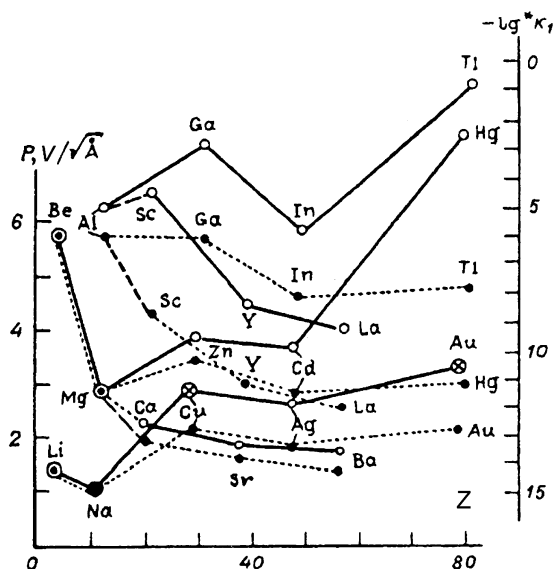


Figure 8. The change of P for free cations (bullets) and of \log^*K_1 for aquocations (open circles) for experimental data, crossed circles for interpolated data) with the increase of atomic number Z . The one, two, and three plus notations have been omitted. Connecting bullets or circles with consecutive Z by thick upward-rising straight lines and joining the ends of those lines with thinner downward-falling lines results in periodic patterns such as those in Figure 7. This figure has been reproduced as Figure 8a–d, Supporting Information, showing the features separately.

on is not evident. The reason: the stability of aquocations $[M(H_2O)_n]^{z+}$ is measured by the energy of binding water to free cations M^{z+} (the hydration energy ΔH_h). In contrast to ΔH_a and ΔH_f the hydration energy ΔH_h does not include the energy expenditure to ionize atom M . (IP values are from ref 29.) On the contrary, the energy ΔH_h to a great degree compensates this expenditure. It happens because the water molecules, joining with the cation M^{z+} , partly replace the electrons which were taken from the atom M . Thus, instead of concomitance between the stability of gaseous compounds and aquocations there is concomitance between the stability of aquocations and the energy expenditure for the corresponding ionization of atoms M (the rule of Bernal and Fowler). For example, note how the last two rows agree but disagree with the first row of Table 2.

Figures 7 and 8 present fragments of the periodic subsystem of aquocations.^{31,32} Figure 7 illustrates the interrelationship between two functions. The first, P ,³³ is the total of the ionization potentials IP of M^{z+} multiplied by $[0.2(\text{cation radius})^{-1/2} \times z^{-0.27}]$. The second is ν_1 , the symmetric vibration frequency of the aquocations,¹⁸ which characterizes the rigidity of the bond between the cation and water. Figure 8 shows the interrelationship between P and the hydrolysis constant logarithm \log^*K_1 ,³¹ which quantifies the hydrolytic ability of cations. The interrelationships are shown by the concomitant change of ν_1 or \log^*K_1 with P as the metal ordinal number Z increases. In Figure 7 the continuous zigzag line demonstrates the periodicity. Similar regularities are seen in Figure 8, obviously illustrating the relation between P and \log^*K_1 . The more the energy expended in the ionization of the metal, the more energetically a metal cation interacts with water, the more rigid are the cation–water bindings, and the deeper is the hydrolytic splitting of water.

Thus, although a change of the conditions under which molecules exist also changes the regularities in their forms

and properties, careful examination of the data in the light of the periodic law allows us to discover the deep relations existing between the regularities.

6. CONCLUSION

The material presented here illustrates the possibility of using the periodic system as a means not only for going from one subsystem of particles to another but also for the qualitative and semiquantitative characterization of the changes of separate subsystems depending on the conditions of their existence.

Supporting Information Available: Figures 7a–d and 8a–d showing the features separately found in Figures 7 and 8, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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