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BINDING D-ELEMENTS OF GROUP VIII OF THE 4TH PERIOD OF THE PERIODIC SYSTEM

Abstract. This article briefly reviews the connecting d-elements of the fourth period I-VIII groups of theperiodic system. Also compares the main elements of the group VIIIA and VIIIB transition group, their properties and electronic formulas.

If we collate the VIIIB subgroup of iron elements with the valence states of argon, krypton VIIIA of the main subgroup, then argon in oxidation rates of 0, +2, +6 is an analog of krypton, and in the oxidation +8 Ar will not be a krypton's analog. On the contrary, in low oxidation rates, iron differs from argon, and in the oxidation of +8, iron is an incomplete analog of argon. Iron is a binder between subgroup VIIIA and subgroup VIIIB by electron configurations with a valence corresponding to the group number of the periodic table.

Gas XeO₄ under ordinary conditions, has not been studied sufficiently, but electron diffraction data and IR spectroscopy indicate that its molecule is tetrahedral. Its structure, based on isomorphism, is similar to the tetrahedral structure of FeO₄, OsO₄, RuO₄.

Key words: transition metals, degree of oxidation, binding element, the terms Klechkovskii, characteristic elements, isomorphism.

In the study of d-elements of the periodic table, it is necessary to focus on their relationship with cpand s- elements. They are called transient and are located in large periods between p- and s- elements, and the ions of which are characterized by one of the $nd^{x}(0 \le x \le 10)$ states (for example, Sc^{3+} - d^{0} , Zn^{2+} - d^{10})

The highest oxidation state of most d-elements corresponds to the group number of the periodic system in which they are located, for example, manifested in oxides:

$$+3$$
 $+4$ $+5$ $+6$ $+7$ $+8$ Sc_2O_3 TiO_2 V_2O_5 CrO_3 Mn_2O_7 FeO_4

Scandium and its analogues in the corresponding periods are the first d-elements. They begin to fill the pre-surface layer. Unlike other d-elements, scandium and its analogues are characterized by the oxidation state +3. In its chemical behavior scandium is similar to aluminum at the same time. The formula of higher scandium oxide- Sc_2O_3 shows the basic properties- $Sc(OH)_3$. Electronic structure of the outer energy layer of scandium is fully consistent with the second rule Kleczkowska. Consequently, its valence electrons are at 4s - and 3d- sublevels. Therefore, the highest degree of oxidation is equal to +3, which corresponds to the group number. And the electronic structure of the atom ends with s-electrons, so this element exhibits metallic properties. The remaining 9 d-elements from IV period are a continuation of the electronic layer. These d-elements in their period are the first d-elements, that is, they begin to fill the d-orbitals, ends at the atom Zn.

The so-called long version of the periodic system proposed by B. V. Nekrasov is often used [1]. In this version, the periods are not divided into parts, but written completely in one line. Similar elements are connected by straight lines. Here it is necessary to compare the oxidation state of the elements

corresponding to the group number of the periodic system. The main achievement of B. V. Nekrasov is that he established Sc, Ti, V, Cr, Mn, Cu, Zn at maximum valence by characteristic elements, but it remains uncertain which elements of the triad are analogs for inert gases at their maximum oxidation state.

However, this cannot be considered a mistake, as the experimental facts at the time was not enough.

In the periodic system, a number of elements are combined into triads (triads of iron, ruthenium and osmium). Inside the triad, the properties of the elements are close. This group includes three of the triad of metals (nine d-elements)

and the noble gases that complete each age. As in any other group, the members of the VIII group can be divided into the main VIIIA - and the side VIIIB – subgroups.

The subgroup of iron includes ruthenium and osmium-each in its period are d-elements, which begins filling the d-orbitals of the previous layer by electron. The maximum oxidation state (+8) is equal to the group number of the periodic table. For iron, the most characteristic oxidation States are +2 and +3, iron derivatives are also known, in which the oxidation state is +4, +6 and +8. There is information about the preparation of iron oxide- $FeO_4(+8)$. This is not a stable volatile compound of pink color[2]. Tetraoxide osmium and ruthenium toxic. Thanks to the acid properties OsO_4 during the interaction with basic compounds:

Vertically, the first d-element of the VIIIB group is iron (IV-th period), followed by ruthenium (V-th period) and osmium (VI-th period). Their electronic configurations of the outer shell of Fe [Ar] $3d^64s^2$, Ru[Kr] $4d^75s^1$ and Os[Xe] $4f^{14}5d^66s^2$ atoms.

Between elements in the vertical columns show some of the features and a closer resemblance. For example, members of the Fe, Ru and Os series are particularly active catalysts in the synthesis of ammonia from hydrogen and nitrogen elements.

If we compare the VIIIB subgroup of iron elements with the valent States of argon, krypton VIIIA of the main subgroup, then argon in the oxidation States 0, +2, +6 is an analogue of krypton, and in the oxidation state +8 Ar will not be an analogue of krypton. In contrast, in the low oxidation States of the iron differs from that of argon, and in the oxidation state +8 iron is incomplete analogue of ar (see tab.1). Electronic configurations of Fe, Ar and Kr in atomic state and oxidation States +2, +6 and +8 (tab.1). Iron is a connecting element between the subgroup VIIIA and the subgroup VIIIBby electronic configurations with valence, corresponding to the group number of the periodic system.

Table 1 -	Comparison (of electroni	c configurations	of iron	aroon and kry	nton as VIII.	-group elements
Table 1 -	Companson	or ciccuoin	c comiguiations	OI HOIL,	argon and Kry	pion as vini.	-group cicinents

Oxidation degree	Fe (VIIIB)	Ar (VIIIA)	Kr (VIIIA)
0	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ⁶ 4s ²	$[1s^22s^22p^6] 3s^23p^6$	$[1s^22s^22p^63s^23p^6] 3d^{10}4s^24p^6$
+2	$\frac{[1s^22s^22p^63s^23p^6]}{3d^6}$	$[1s^22s^22p^6] 3s^23p^4$	$\begin{array}{c} [1s^22s^22p^63s^23p^6] \\ 3d^{10}4s^24p^4 \end{array}$
+6	$\frac{[1s^22s^22p^63s^23p^6]}{3d^2}$	$[1s^22s^22p^6] 3s^2$	
+8	$1s^22s^22p^63s^23p^6$	$1s^22s^22p^6$	

Until recently, it was believed that noble gases were not at all capable of entering into chemical reactions, and placed them in the "zero" group of the periodic table of D.I. Mendeleyev, where the elements with "zero" valency were supposed to be. In 1962 the Canadian chemist N. Bertlett succeeded in obtaining compounds of inert gases with fluorine [3]:

$$Xe + PtF_6Xe^+[PtF_6]^- \longrightarrow$$

Here, PtF6 takes one electron away from xenon. Investigating the chemical properties of the PtF6 compounds of the VIIIB group, N. Bertlett observed that with prolonged exposure to air it changes color, resulting in the formation of O2 + [PtF6] -. The reason for this is that the first ionization energy of xenon is comparable in magnitude to the ionization energy of molecular oxygen (1175 kJ / mol for O2 O2 ++ e-). Therefore, in this case, xenon hexafluoroplatinate is formed similarly to oxohexafluoroplatinate.

A few months later, XeF4 and XeF2 were synthesized in other laboratories [4].

As is known, the degree of oxidation of xenon is (+8) [5].

$$XeO_4 + XeF_6XeO_3F_2 + XeOF_4 \longrightarrow$$

xenon belongs to the VIIIA group.

Tetraoxide is obtained by the action of anhydrous H2SO4 on barox oxoxenate (+8) at room temperature:

$$Ba_2XeO_6+2H_2SO_4 \longrightarrow 2BaSO_4+XeO_4+2H$$

HeO4 under ordinary gas conditions, has not been studied sufficiently, but the data of electron diffraction and IR spectroscopy indicate that its molecule is tetrahedral. Its structure is similar on the basis of isomorphism, the tetrahedral structure of OsO4, RuO4. The derivatives of xenon (+6) are strong oxidants. However, when even more powerful oxidants are applied to them, compounds with a degree of oxidation (+8) can be obtained. Of these compounds, xenon-x-fluoride XeF8, xenonetetraoxide XeO4, and xenonoxodifluoride XeO3F2 are known. These compounds are similar to the acidic compounds OsO4 and RuO4.

The elements of the krypton subgroup-kryptonKr, xenon Xe, radon Rn, are characterized by a lower ionization energy of atoms than the typical elements of neon and argon VIIIB of the group. Therefore, the elements of the krypton subgroup give compounds of the usual type. And in this direction, the elements of the krypton subgroup differ from other noble gases by the large dimensions of the atoms (molecules) and the high polarizability in the series of He-Ne-Ar-Kr-Xe atoms. Due to the high stability of the electronic structure of the atom (ionization energy 15.76 eV), the valence-type compounds for argon have not been obtained.

For He, Ne and Ar, stable compounds are not known [6]. And the next noble gas - krypton has chemical compounds, but their

less than xenon. In addition to KrF2, KrF4, the formation of the first compounds containing Kr-O bonds was detected [7] by NMR spectroscopy (19F, 17O) to monitor the synthesis of the stable compound [Kr (OTeF5) 2]:

$$3KrF_2 + 2B(OTeF_5)_3 \longrightarrow 3Kr(OTeF_5)_2 + 2BF_3$$

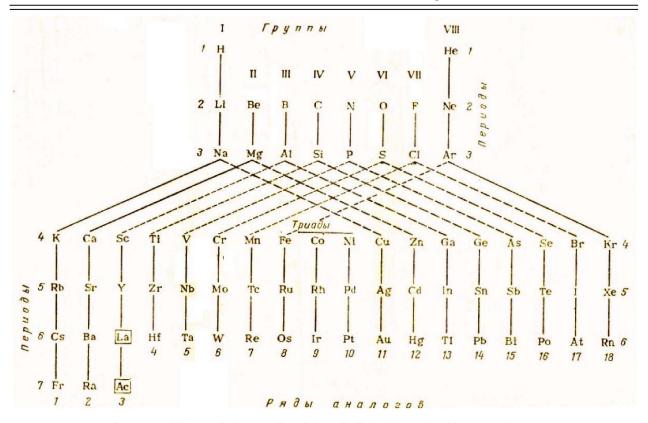


Figure 1 - Addition to the long version of the periodic system proposed by B.V. Nekrasov

Having a relatively larger atomic size, argon is more inclined to form intermolecular bonds than helium and neon. Therefore, the most common clathrates formed by Ar, Kr and Xe with hydroquinone 1,4-C6H4 (OH) 2 and water. Clathrates can serve to store noble gas reserves.

It can be assumed that iron is a link between subgroup VIIIB and subgroup VIIIA at maximum valence (+8). Fe and Ar at maximum valence (+8) are connected by a small dotted line (Fig. 1). For the remaining III, IV, V, VI, VII, I and II groups of the fourth period, the connecting elements are Sc, Ti, V, Cr, Mn, Cu, Zn [1, 8, 9].

Substances formed by elements of the main and secondary subgroups, in some cases, differ in their properties. However, in the highest degree of oxidation, their properties are close. For example, VIIA-subgroup-halogen-oxidizers, VIIB-subgroup-reduction metals, where they exhibit low valence (Cl2O-acidic oxide, MnO-base), the differences were sharply expressed. However, in their highest degree of oxidation, these elements in the composition of the corresponding compounds are similar in properties [9]. Thus, halogens and metals of the VII group oxidize strongly with strong acids: tetraoxochlorate (+7) hydrogen HClO4 and tetraoxomanganate (+7) hydrogen HMnO4, which are also the strongest oxidants.

REFERENCES

- [1] Nekrasov B.V. A textbook of general chemistry (4th ed., Pererab.) Moscow: Khimiya, 1981. 560 p.
- [2] Akhmetov N.S. General and inorganic chemistry. M. High school. 2001. 743p.
- [3] Bartlett N. Proc.Chem.Soc., 218 (1962).
- [4] Claassen H.H., Selig H., Malm J.G. J. Am. Chem. Soc., 84. 3593 (1962).
- [5] Huston J.L. Inorg. Chem., **21**.685-688 (1982)
- [6] Greenwood N., Ernsho A. Chemistry of elements. 2 vol. Moscow: BINOM. Laboratory of knowledge. 2008. 671p.
- [7] J.C.P. Saunders, C.J. Schobilgen. J. Chem. Soc., Chem. Commun., 1576-1578(1989).
- [8] Nasirov R., Matveeva E.F. A comparison in the study of the chemistry of elements // Chemistry in School. 2013. №10.P.49-52.
- [9] Nasirov R. Comparison of p- and d-elements of the VII groups of the periodic system and application of their paramagnetic properties // Reports of NAS RK. 2015. № 4. P. 95-100.

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Д.И.МЕНДЕЛЕЕВТІҢ ПЕРИОДТЫҚ ЖҮЙЕСІНДЕГІІV ПЕРИОДЫНЫҢ БАЙЛАНЫСТЫРУШЫ d -ЭЛЕМЕНТТЕРІ

Аннотация. Мақалада Д.И. Менделеевтің периодтық жүйесінің IV-периодындағы I–VIII топтардың негізгі және қосымша топтарындағы элементтер қарастырылды. Мұнда VIII A негізгі және VIII В қосымша топша элементтерінің электрондық құрылымы және қасиеттері салыстырылды.

Ал, егер VIIIA негізгі тобы элементтері аргонды, криптонды VIIIB тобының элементі темірмен салыстырсак, онда олардың электрондық құрлымын салыстыру нәтежесінде 0, +2, +6 тотығу дәрежелері үшін криптон аргонның аналогы, ал +8 тотығу дәрежесі үшін олар аналог еместігі белгілі. Оған керісінде бұл максимал валенттілікте темір аргонның аналогы. Міне, бұл бізге темір металы VIII A және VIIIB топтарын байланыстырушы элемент екендігіне күмән келтірмейді (+8 тотығу дәрежесінде).

 XeO_4 толығымен зерттелген жоқ, бірақ электронография және ИҚ-спектроскопиялық зерттеулер оның молекуласы изоморфизм негізінде FeO_4 , OsO_4 , RuO_4 сияқты тетраэдрлік құрылымға ие болатындығын көрсетті.

Түйін сөздер: ауыспалы металдар, тотығу дәрежесі,байланыстырушы элемент,Клечковскийдің ережелері,сипаттамалық элементтер, изоморфизм.

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СВЯЗЫВАЮЩИЕ d-ЭЛЕМЕНТЫ I-VIII ГРУППЫ 4-ГО ПЕРИОДА ПЕРИОДИЧЕСКОЙ СИСТЕМЫ Д.И.МЕНДЕЛЕЕВА

Аннотация. В статье вкратце рассматривается связывающие d-элементы четвертого периода I-VIII группы периодической системы Д .И. Менделеева. Сравниваются элементы VIIIA главной группы и VIIIB побочной группы, их электронные формулы и свойства.

Если сопоставить VIIIВ подгруппу элементов железа с валентными состояниями аргона, криптона VIIIА главной подгруппы, то аргон в степенях окисления 0, +2, +6 является аналогом криптона, а в степени окисления +8 Аг не будет аналогом криптона. Напротив, в низких степенях окисления железо отличается от аргона, а в степени окисления +8 железо является неполным аналогом аргона. Железо является как бы связующим элементом между подгруппой VIIIА и подгруппой VIIIВ по электронным конфигурациям при валентности, отвечающей номеру группы периодической системы.

 XeO_4 в обычных условиях газ, изучен пока недостаточно, но данные электронографии и ИК-спектроскопии указывают на то, что его молекула тетраэдрическая. Его строение аналогично на основе изоморфизма, тетраэдрическому строению FeO_4 , OsO_4 , RuO_4 .

Ключевые слова: переходные металлы, степень окисление, связывающий элемент, правила Клечковского, характеристические элементы, изоморфизм.

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