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A Nearly Complete System of Average Crystallographic Ionic Radii and Its Use for Determining Ionization Potentials

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Abstract—Available systems of empirical (crystallographic) ionic radii are compared. All these systems turn out to be compatible if the O^{2-} radius is taken to be 0.140 nm. The choice of the oxygen ionic radius is dictated by the equality of the metal ion–oxygen ion distances in oxide crystals and the metal ion–oxygen atom distances in crystal hydrates and concentrated aqueous solutions. In all systems of empirical ionic radii under consideration, the uncertainty of determination of ionic radii is 0.002–0.005 nm. A new method of determination of the ionic radii of elements in unusual valence states is suggested: from the empirical dependence of the electron density at an atom in a given valence state on the atomic radius, a two-parameter equation relating the ionic radii of Period 4–7 elements in two valence states is derived, which allows one to calculate the ionic radius that cannot be determined by crystallography because of the lack of stable compounds in this valence state. Ionic radii are calculated for all Period 4–7 elements in all valence states. They constitute a nearly complete system of ionic radii. There is a linear relationship between the atomic nucleus charge and the inverse ionic radius. It is shown that the square root of the ionization potential is a linear function of the inverse ionic radius. The as yet experimentally unknown ionization potentials of 78 ions of different elements are estimated.

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The idea of atoms as rigid spheres dates back to ancient times. At the end of the 19th century, this concept was extended to ions in crystals. In 1898, the radii of a few ions were determined [1]. Only the advent of X-ray crystallography made it possible to experimentally determine interatomic distances and, hence, atomic and ionic radii. The concepts of atomic, ionic, and van der Waals radii have been developed, and methods of their determination and areas of their reasonable use in crystallography and solid state chemistry have been found [2–16].

In the present study, we consider the available data on ionic radii. Of all types of radii (ionic, covalent, metallic), we select ionic radii since they provide the simplest way to estimate the average valence electron density in ionic crystals, which makes it possible to consider the properties of crystals not only along the periods or groups of the periodic table but also across the table as a whole, assuming that atoms and ions are soft spheres [17–19].

There are several tens of large and small systems of ionic radii determined by different methods and suggested by various authors. The total number of valence states of elements for which ionic radii have been experimentally found is about 200 of the approximately 400 theoretically possible states (including ionic radii of unstable valence states for which stable chemical compounds and, hence, X-ray crystallographic data on interatomic distances cannot be obtained). Ionic radii are usually used for semiquantitative estimation of interatomic distances in crystallographic studies. However, if there existed a unified system of ionic radii, they would also be used for quantifying the average valence electron density in simple compounds (which is used for comparing the properties of solid and liquid metals [18, 19]), finding ionization potentials (as shown in [20]), revealing the structure of radiation defects [17], determining the ionic radii of elements in unstable valence states (such valence states are encountered as intermediate in different chemical processes), studying the electronic structure of solids by the sublattice method [21], and solving many other problems. However, none of the suggested systems of radii contains all known ionic radii even for one coordination number (the largest number of ionic radii was determined for CN = 6), whereas quantitative estimation requires a unified complete table of ionic radii for all possible valence states, including unstable ones. The situation with ionic radii is generally the same as that with covalent and van der Waals radii, which were used only for semiquantitative estimation until [15, 16]. The understanding of this circumstance (we are engaged in studying the properties of compounds as a function of the

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Table 1. Comparison of interatomic cation–water and anion–water distances d in liquid solutions and solid crystal hydrates and cation–oxygen distances in oxides (CN = 6; if it differs from 6, it is parenthesized). The d values were rounded to the third decimal place. The average values are 0.99 ± 0.03 and 0.99 ± 0.05

No.	Ion	d in solution, nm (d_s)	d in crystal hydrate, nm (d_c)	d in oxide, nm (d_o)	d_s/d_c	d_s/d_o
3	Li^+	0.208 ± 0.007 (5.2 ± 0.8)	0.212 ± 0.002	–	0.98 ± 0.04	–
4	Be^{2+}	–	0.164 (4)	0.164 (4)	–	0.99 ± 0.03
9	F^-	0.263 ± 0.002 (6.0 ± 1.0)	0.269 ± 0.005	–	0.98 ± 0.03	–
11	Na^+	0.236 ± 0.006 (5.9 ± 1.0)	0.244 ± 0.003	–	0.97 ± 0.04	–
12	Mg^{2+}	0.209 ± 0.004 (6.2 ± 0.8)	0.207 ± 0.003	0.210	1.01 ± 0.03	0.99 ± 0.04
13	Al^{3+}	0.189 ± 0.002	0.189 ± 0.002	0.190	1.00 ± 0.01	1.00 ± 0.04
17	Cl^-	0.319 ± 0.007 (6.2 ± 0.8)	0.319	–	1.00 ± 0.03	–
19	K^+	0.280 ± 0.008 (6.5 ± 0.9)	0.280 ± 0.009	–	0.97 ± 0.06	–
20	Ca^{2+}	0.242 ± 0.005 (7.1 ± 1.2)	0.241 (7)	0.243 (7)	1.04 ± 0.04	1.00 ± 0.05
24	Cr^{3+}	0.197 ± 0.003 (5.9 ± 0.3)	0.196 ± 0.006	–	1.00 ± 0.05	–
25	Mn^{2+}	0.219 ± 0.002 (5.4 ± 0.6)	0.219 ± 0.001	–	1.00 ± 0.03	–
26	Fe^{2+}	0.211 ± 0.001 (5.8 ± 0.4)	0.213 ± 0.002	0.214	0.99 ± 0.02	0.99 ± 0.03
27	Co^{2+}	0.211 ± 0.002 (5.8 ± 0.4)	0.211 ± 0.002	0.213	1.00 ± 0.02	0.99 ± 0.03
28	Ni^{2+}	0.206 ± 0.002 (6.0 ± 0.6)	0.208 ± 0.004	0.209	0.99 ± 0.03	0.99 ± 0.03
29	Cu^{2+}	0.211 (3.8 ± 1.5)	0.212 ± 0.004	0.208	0.99 ± 0.02	1.01 ± 0.03
30	Zn^{2+}	0.210 ± 0.007 (5.5 ± 1.3)	0.210 ± 0.003	0.209	1.00 ± 0.05	1.00 ± 0.03
37	Rb^+	0.289	0.299 ± 0.007	–	0.97 ± 0.04	–
38	Sr^{2+}	0.262 ± 0.002 (8.0 ± 0.1)	0.262 ± 0.002	0.266	1.00 ± 0.02	0.98 ± 0.03
39	Y^{3+}	0.236 (8.0)	0.240 (9)	0.238 (9)	0.97 ± 0.03	0.99 ± 0.03

electron density of their constituent elements) compelled us to critically survey the available data on ionic radii.

All systems of ionic radii can be divided into three groups: empirical, semiempirical, and theoretical. The first group, empirical ionic radii, comprises the radii calculated from interatomic distances. Interatomic distances are determined by X-ray or neutron diffraction; however, other approaches are also possible, for example, calculation based on the lattice energy [22]. Then, the value of the reference ionic radius was selected for some element, for example, oxygen or fluorine, and the radii of other ions are found by subtracting the reference radius from the corresponding interatomic distances.

In semiempirical methods, reference ionic radius values are selected for several ions taken from a radius system from the first group and the radii of other elements in various stable valence states are determined using the dependence of a physical or chemical property on the nucleus charge, valence state, ionization potential, etc. (the radii of unstable valence states can also be estimated).

The third group, theoretical ionic radii (they are also referred to as orbital), includes radii obtained by quantum-chemical calculations.

A large body of data on radius determination is available (see, for example, reviews [11, 23]). However, here we consider only empirical ionic radii, which are directly related to experimental interatomic distances. Available ionic radii obtained by different researches will be treated as independent experimental data and will be used in statistical processing with the same statistical weights.

Interatomic (interionic, internuclear) distances are determined by X-ray diffraction as the distances between the centers of gravity of a pair of atoms or ions. To go from interatomic distances to ion sizes (crystallographic radii of ions or ionic radii), the interatomic distance should be divided between the cation and anion. Researchers have solved this problem differently. In particular, radii were found assuming the existence of an anion–anion contact [3], on the basis of refraction data [4], using the ratio of effective charges in halides [6, 7], etc. These methods were used for determining the radii of reference ions, and the remaining radii can be found by subtracting these reference values from the other interatomic distances. It is worth noting that the radii of the reference ion determined by different researchers were rather different (for example, for doubly charged oxygen ions, these values ranged from 0.132 to 0.156 nm). These differences, as well as different sets of initial interatomic distances and different statistical processing procedures, were responsible for the invention of inconsistent systems of ionic radii.

It is natural that such a large scatter of ionic radius values prevented their use for quantitative treatment. It was necessary to compose a unified table referred to

Table 2. Average values of empirical (crystallographic) ionic radii of Period 2 and 3 elements for CN = 6

No.	Element	Valence state	*R*, nm	No.	Element	Valence state	*R*, nm
1	H	–1	0.165 ± 0.028	11	Na	+1	0.098 ± 0.004
3	Li	+1	0.070 ± 0.006	12	Mg	+2	0.071 ± 0.003
4	Be	+2	0.035 ± 0.007	13	Al	+3	0.051 ± 0.003
5	B	+3	0.022 ± 0.005	14	Si	+4	0.040 ± 0.004
6	C	+4	0.016 ± 0.004			–4	0.239 ± 0.033
		–4	0.260	15	P	+5	0.030 ± 0.007
7	N	+5	0.011 ± 0.003			+3	0.044
		+3	0.016		P	–3	0.211 ± 0.016
		–3	0.172 ± 0.022	16	S	+6	0.027 ± 0.002
8	O	+6	0.008 ± 0.002			+4	0.037
		–2	0.140 ± 0.002			–2	0.186 ± 0.004
9	F	+7	0.006 ± 0.002	17	Cl	+7	0.024 ± 0.002
		–1	0.134 ± 0.004			–1	0.183 ± 0.005

one radius value. It was suggested in [24] that different systems of ionic radii are consistent with one another if comparison is based on the same reference radius. Thus, it is necessary to choose a definite value of the reference radius. It is likely that the best choice is the ionic radius of the doubly charged oxygen ion (or fluoride ion) since the covalent contributions to the interatomic distances in oxides and fluorides are minimal (for example, it is noticeable in the case of sulfides).

To date, interatomic distances have been measured for a vast number of inorganic compounds. In particular, the water–cation and water–anion distances have been determined in crystal hydrates [25] and concentrated aqueous solutions [26]. Since the size of the O^{2-} ion should be close to the size of the water molecule (this follows, for example, from the fact that the M···M distances are close in crystal hydrates and oxides [27, 28]), it is expedient to compare the cation–water (cation–water oxygen) distances in solutions and crystal hydrates and the cation–oxygen distance in oxides. The interatomic distances in oxides were taken from [29]. The results of comparison are summarized in Table 1. As is seen, the interatomic distances in the three classes of compounds are the same within the error of determination. The same interatomic distances in crystal hydrates and oxides were reported for the first time in [29]. The same size of water molecules and O^{2-} ions allows us to assume that the radius of this ion is the same as the water molecule radius. This radius is known for both liquid water and ice: 0.138–0.142 nm [26, 29]. Therefore, it can be assumed that the average radius of the doubly charged oxygen ion is 0.140 ± 0.002 nm. This value was used in [6, 7] and in [13, 14].[1]

[1] In these works, the authors presented tables of ionic radii of different elements for two reference ions (oxygen and fluorine), which differ by 0.014 nm. Without any discussion of this difference, only the set based on the oxygen ions was considered.

Of all sources of information on empirical crystallographic ionic radii for CN = 6, we selected 13 works where radii were crystallographically determined for the largest number of ions [4, 5, 7–9, 12–14, 20, 30–33]. Radius values to the third decimal place (in nm) were used. The mean geometric error was estimated (in some works, the radius values are given with a four decimal place accuracy; however, as follows from the scatter of radius values, this accuracy is artificial).The radii obtained for Period 2 and 3 elements are summarized in Table 2. The ionic radii for Period 4–7 elements are listed in Tables 3 and 4 (in roman type). The lanthanide ionic radii were obtained by averaging the values reported in [5, 6, 9, 13, 14, 25, 32–39], and the actinide radii were obtained by averaging the values taken from [5, 6, 9, 13, 14, 23, 33, 34, 36, 37, 40, 41]. All radii were reduced to the oxygen ion radius (0.140 nm) by subtracting this value from the sum of the cation and anion radii. As follows from Table 2, the average radii (nm) obtained by various researchers differ only by a few units in the third decimal place for cations and doubly and singly charged anions. For triply charged anions, the difference is rather noticeable. The radii of quadruply charged anions were determined in few works; therefore, their values are unreliable. Our system of average crystallographic radii is closest to the system of effective ionic radii in which the ionic radii are given relative to the doubly charged oxygen atom [13, 14]. Inasmuch as the system of average crystallographic radii was based on the data of many authors, our system turned out to be more complete than the system of radii presented in [13, 14].

Comparison of selected interatomic distances with the sums of the corresponding ionic radii and comparison with the sums of effective radii showed that, for halides, oxides, sulfides, selenides, and tellurides, the experimental interatomic distances are consistent with

Table 3. Complete system of ionic radii of Period 4–7 elements. The literature calculated values of average crystallographic ionic radii are given in roman type, and the ionic radii for unstable valence states calculated in this work as described below are italicized

Element	Valence state								
	0	+1	+2	+3	+4	+5	+6	+7	+8
	Ionic radius, nm								
1	2	3	4	5	6	7	8	9	10
K	0.234	0.132 ± 0.004							
Ca	0.197	*0.130*	0.100 ± 0.003						
Sc	0.164	*0.120 ± 0.012*	*0.086 ± 0.005*	0.076 ± 0.003					
Ti	0.145	*0.104 ± 0.002*	0.080 ± 0.006	0.066 ± 0.003	0.062 ± 0.003				
V	0.135	*0.097 ± 0.003*	0.074 ± 0.006	0.063 ± 0.003	0.058 ± 0.004	0.047 ± 0.010			
Cr	0.128	*0.095 ± 0.006*	0.080 ± 0.002	0.061 ± 0.001	0.053 ± 0.006	0.049	0.038 ± 0.010		
Mn	0.130	*0.101 ± 0.006*	0.083 ± 0.002	0.062 ± 0.002	0.050 ± 0.004	*0.046 ± 0.002*	*0.041 ± 0.002*	0.036 ± 0.008	
Fe	0.127	*0.094 ± 0.001*	0.076 ± 0.002	0.062 ± 0.003	0.052 ± 0.003	*0.045 ± 0.002*	*0.039 ± 0.002*	*0.037 ± 0.003*	*0.031 ± 0.003*
Co	0.126	*0.090 ± 0.003*	0.074 ± 0.002	0.059 ± 0.005	0.051 ± 0.002	*0.044 ± 0.002*	*0.038 ± 0.002*	*0.034 ± 0.002*	*0.030 ± 0.003*
Ni	0.124	*0.091 ± 0.005*	0.071 ± 0.003	0.062 ± 0.003	0.051 ± 0.003	*0.044 ± 0.002*	*0.039 ± 0.002*	*0.034 ± 0.002*	*0.030 ± 0.002*
Cu	0.128	*0.095 ± 0.001*	0.075 ± 0.002	*0.062 ± 0.001*	–	–	–	–	–
Zn	0.137	*0.097 ± 0.002*	0.076 ± 0.002	–	–	–	–	–	–
Ga	0.139	*0.100*	*0.079 ± 0.001*	0.063 ± 0.004	–	–	–	–	–
Ge	0.139	*0.100*	0.072 ± 0.006	*0.064 ± 0.005*	0.052 ± 0.007	–	–	–	–
As	0.140	*0.100 ± 0.005*	*0.075 ± 0.005*	0.064 ± 0.006	*0.056 ± 0.003*	0.047 ± 0.003	–	–	–
Se	0.117	*0.085 ± 0.018*	*0.069 ± 0.005*	*0.059 ± 0.005*	0.054 ± 0.006	*0.044 ± 0.002*	0.038 ± 0.005	–	–
Br	0.114	*0.086*	*0.071 ± 0.002*	*0.059 ± 0.002*	*0.051 ± 0.003*	*0.044 ± 0.002*	*0.038 ± 0.003*	*0.034 ± 0.003*	–
Rb	0.253	0.148 ± 0.005	–	–	–	–	–	–	–
Sr	0.216	–	0.116 ± 0.003	–	–	–	–	–	–
Y	0.118	*0.116*	*0.096*	0.087 ± 0.005	–	–	–	–	–
Zr	0.160	*0.114*	*0.087 ± 0.007*	*0.079 ± 0.005*	0.072 ± 0.007				
Nb	0.140	*0.109 ± 0.018*	*0.098 ± 0.004*	0.078 ± 0.003	*0.070 ± 0.006*	0.064 ± 0.004	–	–	–
Mo	0.140	*0.105 ± 0.015*	*0.089 ± 0.005*	0.078 ± 0.006	0.068 ± 0.004	0.063 ± 0.004	0.058 ± 0.005	–	–
Tc	0.136	*0.109 ± 0.004*	*0.089 ± 0.003*	*0.079 ± 0.002*	0.068 ± 0.005	0.065 ± 0.004	*0.062 ± 0.004*	0.058 ± 0.005	–
Ru	0.132	*0.104*	0.087 ± 0.003	0.075 ± 0.001	0.067 ± 0.003	*0.061 ± 0.004*	*0.058 ± 0.003*	0.054 ± 0.003	*0.051 ± 0.003*
Rh	0.134	*0.105*	*0.087 ± 0.002*	0.078 ± 0.002	0.068 ± 0.004	0.063 ± 0.004	*0.058 ± 0.004*	*0.054 ± 0.003*	*0.052 ± 0.003*
Pd	0.134	*0.107*	0.087 ± 0.004	0.078 ± 0.003	0.068 ± 0.004	*0.063 ± 0.004*	*0.059 ± 0.004*	*0.055 ± 0.004*	*0.053 ± 0.004*
Ag	0.145	0.110 ± 0.009	0.089 ± 0.003	0.074 ± 0.006	–	–	–	–	–
Cd	0.152	*0.116 ± 0.004*	0.090 ± 0.005	–	–	–	–	–	–
In	0.157	0.121 ± 0.009	*0.088 ± 0.006*	0.081 ± 0.004	–	–	–	–	–
Sn	0.158	*0.112 ± 0.007*	0.095 ± 0.003	*0.081 ± 0.004*	0.072 ± 0.005	–	–	–	–
Sb	0.161	*0.114*	*0.095*	0.082 ± 0.003	*0.075 ± 0.004*	0.062 ± 0.005	–	–	–
Te	0.137	*0.107*	*0.089 ± 0.002*	*0.079 ± 0.002*	0.075 ± 0.004	*0.067 ± 0.004*	0.056 ± 0.004	–	–
I	0.133	*0.102 ± 0.003*	*0.085 ± 0.004*	*0.075 ± 0.004*	*0.067 ± 0.004*	0.062 ± 0.004	*0.058 ± 0.004*	0.053 ± 0.004	–
Cs	0.274	0.165 ± 0.006	–	–	–	–	–	–	–
Ba	0.225	*0.166 ± 0.007*	0.137 ± 0.005	–	–	–	–	–	–

Table 3. (Contd.)

1	2	3	4	5	6	7	8	9	10
La	0.186	*0.148 ± 0.009*	0.120 ± 0.007	0.104 ± 0.008	–	–	–	–	–
Ce	0.182	*0.149 ± 0.009*	*0.120 ± 0.006*	0.102 ± 0.006	0.088 ± 0.006	–	–	–	–
Pr	0.182	*0.149 ± 0.009*	*0.120 ± 0.006*	0.102 ± 0.006	0.088 ± 0.05	–	–	–	–
Nd	0.182	*0.144 ± 0.005*	*0.117 ± 0.004*	0.100 ± 0.005	0.085 ± 0.003	–	–	–	–
Pm	0.181	*0.142 ± 0.003*	*0.115 ± 0.002*	0.097 ± 0.004	0.085 ± 0.003	–	–	–	–
Sm	0.181	*0.141 ± 0.009*	0.112 ± 0.005	0.097 ± 0.005	0.084 ± 0.004	–	–	–	–
Eu	0.202	*0.147 ± 0.004*	0.118 ± 0.004	0.099 ± 0.005	*0.087 ± 0.002*	–	–	–	–
Gd	0.179	*0.140 ± 0.002*	*0.114 ± 0.002*	0.096 ± 0.006	0.084 ± 0.002	–	–	–	–
Tb	0.177	*0.136 ± 0.003*	*0.111 ± 0.004*	0.094 ± 0.006	0.081 ± 0.004	–	–	–	–
Dy	0.177	*0.132 ± 0.005*	*0.106 ± 0.006*	0.092 ± 0.006	0.081 ± 0.004	–	–	–	–
Ho	0.176	*0.133 ± 0.004*	*0.110 ± 0.005*	0.093 ± 0.004	0.081 ± 0.004	–	–	–	–
Er	0.175	*0.132 ± 0.004*	*0.109 ± 0.004*	0.092 ± 0.004	0.080 ± 0.004	–	–	–	–
Tm	0.174	*0.130 ± 0.006*	0.108 ± 0.005	0.092 ± 0.005	*0.081 ± 0.006*	–	–	–	–
Yb	0.193	*0.145*	0.109 ± 0.008	0.092 ± 0.007	*0.083 ± 0.005*	–	–	–	–
Lu	0.174	*0.130 ± 0.005*	*0.108 ± 0.005*	0.091 ± 0.005	*0.083 ± 0.005*	–	–	–	–
Hf	0.156	*0.124 ± 0.003*	*0.104 ± 0.004*	*0.090 ± 0.004*	0.077 ± 0.004	–	–	–	–
Ta	0.146	*0.119 ± 0.010*	*0.100 ± 0.008*	0.087 ± 0.002	*0.075 ± 0.005*	0.061 ± 0.005	–	–	–
W	0.141	*0.112 ± 0.010*	*0.095 ± 0.007*	*0.083 ± 0.005*	0.074 ± 0.004	0.066 ± 0.005	0.059 ± 0.004	–	–
Re	0.137	*0.100 ± 0.007*	*0.094 ± 0.004*	*0.082 ± 0.004*	0.069 ± 0.006	0.062 ± 0.005	0.055 ± 0.006	0.053 ± 0.006	–
Os	0.134	*0.112*	0.092 ± 0.007	0.080 ± 0.004	0.068 ± 0.006	0.064 ± 0.004	0.058 ± 0.003	0.053 ± 0.003	0.048 ± 0.003
Ir	0.135	*0.112*	0.092 ± 0.005	0.081 ± 0.005	0.070 ± 0.005	0.063 ± 0.004	*0.057 ± 0.004*	*0.052 ± 0.004*	*0.048 ± 0.004*
Pt	0.138	*0.114*	0.097 ± 0.002	*0.083 ± 0.005*	0.070 ± 0.005	0.064 ± 0.004	*0.059 ± 0.004*	*0.053 ± 0.004*	*0.049 ± 0.004*
Au	0.144	0.136 ± 0.002	*0.099 ± 0.004*	0.085 ± 0.004	*0.076 ± 0.002*	0.068 ± 0.002	–	–	–
Hg	0.155	0.124 ± 0.006	0.103 ± 0.004	–	–	–	–	–	–
Tl	0.171	0.138 ± 0.002	*0.112 ± 0.004*	0.095 ± 0.005	–	–	–	–	–
Pb	0.174	*0.136 ± 0.008*	0.113 ± 0.005	*0.097 ± 0.003*	0.082 ± 0.005	–	–	–	–
Bi	0.182	*0.148 ± 0.010*	*0.117 ± 0.005*	0.102 ± 0.007	*0.086 ± 0.005*	0.075 ± 0.005	–	–	–
Po	0.207 ± 0.020	*0.157 ± 0.010*	*0.123 ± 0.004*	*0.104 ± 0.005*	0.089 ± 0.005	*0.079 ± 0.003*	0.069 ± 0.003	–	–
At	0.228 ± 0.020	*0.170 ± 0.010*	*0.134 ± 0.006*	*0.109 ± 0.005*	*0.092 ± 0.003*	*0.080 ± 0.002*	*0.069*	0.062	–
Fr	0.280	0.181	–	–	–	–	–	–	–
Ra	0.235	–	0.141	–	–	–	–	–	–
Ac	0.203	*0.155 ± 0.004*	*0.129 ± 0.002*	0.109 ± 0.004	–	–	–	–	–
Th	0.180	*0.144 ± 0.009*	*0.123 ± 0.005*	0.104 ± 0.003	0.094	–	–	–	–
Pa	0.162	*0.138 ± 0.007*	*0.117 ± 0.005*	*0.104 ± 0.004*	0.091 ± 0.006	0.086 ± 0.007	–	–	–
U	0.153	*0.130 ± 0.010*	*0.109 ± 0.006*	0.100 ± 0.006	0.089 ± 0.006	0.082 ± 0.006	0.076 ± 0.007	–	–
Np	0.150	*0.134 ± 0.15*	0.110 ± 0.009	0.099 ± 0.008	0.089 ± 0.006	0.084 ± 0.008	0.076 ± 0.007	0.071 ± 0.004	–
Pu	0.162	*0.129 ± 0.015*	*0.115 ± 0.007*	0.100 ± 0.006	0.088 ± 0.004	0.082 ± 0.008	0.076 ± 0.006	*0.072 ± 0.004*	–
Am	0.184	*0.144 ± 0.015*	*0.121 ± 0.012*	0.097 ± 0.005	0.092 ± 0.005	0.082 ± 0.004	0.076 ± 0.005	*0.072 ± 0.003*	–
Cm	0.164 ± 0.006	*0.133 ± 0.005*	*0.114 ± 0.003*	0.098 ± 0.003	0.089 ± 0.004	*0.080 ± 0.004*	*0.075 ± 0.004*	–	–
Bk	0.151 ± 0.006	*0.125 ± 0.004*	*0.108 ± 0.003*	0.098 ± 0.003	0.089 ± 0.004	*0.080 ± 0.004*	*0.075 ± 0.004*	–	–
Cf	0.137 ± 0.010	*0.116 ± 0.007*	*0.102 ± 0.005*	0.095 ± 0.004	0.083 ± 0.004	*0.079 ± 0.003*	*0.075 ± 0.002*	–	–

Table 4. Comparison of ionic radii R_i in crystal and solution and thermochemical radii R_t of some element for CN = 6

No.	Ion	R_i in crystal, nm	R_i in solution, nm	R_t, nm
1	H^-	0.165 ± 0.028	–	0.173 ± 0.020
3	Li^+	0.070 ± 0.006	0.071 ± 0.007	–
8	O^{2-}	0.140	–	0.149 ± 0.008
9	F^-	0.134 ± 0.004	0.124 ± 0.003	0.126 ± 0.003
11	Na^+	0.098 ± 0.005	0.097 ± 0.006	–
12	Mg^{2+}	0.071 ± 0.005	0.070 ± 0.004	–
13	Al^{3+}	0.052 ± 0.005	0.050 ± 0.002	–
16	S^{2-}	0.186 ± 0.006	–	0.191 ± 0.007
17	Cl^-	0.183 ± 0.008	0.180 ± 0.007	0.172 ± 0.005
19	K^+	0.132 ± 0.006	0.141 ± 0.008	–
20	Ca^{2+}	0.100 ± 0.003	0.103 ± 0.005	–
24	Cr^{3+}	0.061 ± 0.001	0.058 ± 0.003	–
25	Mn^{2+}	0.083 ± 0.002	0.080 ± 0.001	–
26	Fe^{3+}	0.064 ± 0.003	0.064 ± 0.002	–
27	Co^{2+}	0.074 ± 0.001	0.072 ± 0.001	–
28	Ni^{2+}	0.070 ± 0.002	0.067 ± 0.001	–
29	Cu^{2+}	0.075 ± 0.002	0.072	–
30	Zn^{2+}	0.076 ± 0.002	0.070 ± 0.007	–
34	Se^{2-}	0.198 ± 0.003	–	0.209 ± 0.004
35	Br^-	0.198 ± 0.006	0.198 ± 0.005	0.188 ± 0.006
37	Rb^+	0.148 ± 0.004	0.150	–
38	Sr^{2+}	0.116 ± 0.004	0.125	–
39	Y^{3+}	0.092 ± 0.004	0.097	–
44	Rh^{3+}	0.066 ± 0.004	0.065 ± 0.001	–
47	Ag^+	0.115 ± 0.007	0.102 ± 0.002	–
48	Cd^{2+}	0.096 ± 0.003	0.102 ± 0.002	–
49	In^{3+}	0.082 ± 0.003	0.076 ± 0.001	–
50	Sn^{2+}	0.096 ± 0.002	0.94	–
52	Te^{2-}	0.218 ± 0.007	–	0.220 ± 0.008
53	I^-	0.223 ± 0.006	0.225 ± 0.004	0.210 ± 0.008
55	Cs^+	0.166 ± 0.006	0.173 ± 0.008	–
57	La^{3+}	0.106 ± 0.006	0.114 ± 0.005	–
81	Tl^{3+}	0.092 ± 0.005	0.084 ± 0.001	–
85	At^-	0.221	–	0.222

the values calculated from the sums of ionic radii. The system of average crystallographic radii provides an even more accurate description of interatomic distances than the system of effective radii. For nitrides, arsenides, and hydrides, the interatomic distances, while coinciding with the sums of ionic radii within the error of determination, tend to be shorter than the sum of the corresponding radii. This can be due to an insufficient accuracy of determination of these anionic radii, as well as due to a noticeable covalent contribution to the bond of these ions. For carbides, the calculated values are considerably larger than the experimental ones. If the concepts of ionic radii are extended to triply and quadruply charged anions, their radii should be redetermined. As a whole, the table of average crystallographic radii even in the full (nonminimized) form can be used as a basis for determining ionic radii of unusual valence states, which is described below.

It is also worth noting that, as expected in [26], the average crystallographic ionic radius coincides, within the error of determination, with the ionic radius (Table 4) found in solutions for CN = 6, as well as with the radius found by thermochemical methods [42].

Few studies are available in which the ionic radii were determined for unstable valence states of elements. In particular, the radii of positive monatomic ions were calculated in [43] by an equation containing

three parameters that can be found from the known ionic radii. In [43], the system of ionic radii from [5] was used for calculations. In [44], the radii of positive and negative ions in different valence states were calculated through the Bohr radii of atoms, assuming that all atoms are hydrogen-like, according to [7], and taking into account the shielding of electrons and the degree of polarity. The equations used in calculations contain three parameters, which should be determined independently of each other. In [45], an incomplete table of radii of positive ions in unstable valence states was composed with the use of internal correlations. This system is based on a somewhat modified system of ionic radii [9]. In [20], on the basis of the notions of [6, 7], an expression with four parameters was obtained, which were used for calculating the ionic radii for many unstable valence states. The radii of some valence states were also estimated in [33, 40, 46–52]. Comparison of the radii of ions in unstable valence states obtained by different researchers was not carried out, and the error of determination of the ionic radius has never been estimated.

Thus, the question of the radii of ions in unstable valence state is still open. In this work, we attempted to solve this problem by studying the relation between ionic radii and the average valence electron density.

In [18], for comparison of the physicochemical properties of metals, the notion of average valence electron density ρ was used. The density is defined as follows:

$$\rho = n/(V_a - V_i), \quad (1)$$

where n is the number of valence electrons lost in transition from a neutral atom to a given ion or from one ion to another, V_a is the volume of the atom, and V_i is the volume of the ion (or the volume of the previous and subsequent ions, respectively). To calculate the average electron density, we use the average crystallographic ionic radii R presented in Table 3 (in roman type); the atomic radii were taken from [53]. The average valence electron density was calculated not only for an atom–ion pair but also for pairs of ions in which the first ion had lower valence (lower charge) than the second ion. This allowed us to increase the number of values of the average valence electron density for each n value. It was found that the logarithm of average electron density depends linearly on the logarithm of the radius of an atom or larger ion. This relationship is described by the simple equation

$$\ln\rho = a - m\ln R_a, \quad (2)$$

where R_a is the radius of an atom (or of an ion with lower charge), and a and m are constants for each n value. The substitution of Eq. (1) into Eq. (2) and exponentiation gives the following equation for the unknown ionic radius R_i (the radius of the ion whose volume was determined above):

$$R_i^3 = R_a^3 - bR_a^m, \quad (3)$$

where $b = 3n/4\pi e^a$. As distinct from the previous equations, this equation contains only two, rather than three or four, empirical parameters. In addition, in contrast to [20, 43, 44], calculation of radii by this method does not require any assumptions on the structure and physicochemical properties of atoms.

Table 5. Parameters of Eq. (3) for various n's

Period	n	m	a	Number of points	σ^2
4	1	–3.51	–0.793	21	0.4
	2	–3.40	–0.384	23	1.27
	3	–3.11	–0.153	15	0.14
	4	–3.13	0.438	11	0.26
5	1	–4.18	–0.148	16	0.17
	2	–3.98	–0.184	22	0.07
	3	–4.23	0.283	13	0.05
	4	–3.18	0.053	10	0.007
6	1	–3.83	–0.329	22	0.14
	2	–3.46	–0.184	19	0.09
	3	–3.39	0.061	22	0.007
	4	–2.8	0.047	14	0.003
7	1	–4.14	–0.072	18	0.14
	2	–4.26	0.258	14	0.19
	3	–3.67	0.269	14	0.03
	4	–3.86	0.558	8	0.003

Table 6. Parameters of Eq. (5) for various n's

Period	n	m	a	Number of points	σ^2
4	1	–4.39	–1.84	21	0.40
	2	–4.41	–2.43	23	0.50
5	1	–5.02	–1.44	16	0.45
	2	–5.33	–2.05	22	0.80
6	1	–4.39	–1.11	22	1.27
	2	–4.43	–1.63	19	0.69
7	1	–5.47	–0.796	18	0.30
	2	–6.23	–0.905	14	0.60

The a and m parameters are listed in Table 5. It is worth noting that the parameters change rather smoothly in going from $n = 1$ to $n = 4$. At the same time, at high values $n \geq 5$, the number of points is insufficient for reliable calculation of the parameters of Eq. (3) and, hence, the radius of the ion in an unstable valence state. We may construct the plots of the average valence electron density not only versus the radius of a larger ion (atom) but also versus the radius of a smaller ion. The

Table 7. Example of calculation of average crystallographic radii for titanium ions by Eq. (3). The initial valence state is parenthesized

Valence states though which the calculation was performed	Valence state	Calculation radius, nm	Average calculated radius, nm	Average crystallographic radius, nm
(0), 1	+1	0.104	0.104	–
(0), 1, 1	+2	0.080	0.080 ± 0.001	0.080 ± 0.006
(0), 2		0.081		
(1), 1		0.080		
(0), 1, 1, 1	+3	0.065	0.066 ± 0.001	0.066 ± 0.002
(0), 1, 2		0.066		
(0), 2, 1		0.065		
(0), 3		0.074		
(1), 1, 1		0.065		
(1), 2		0.068		
2, 1		0.065		
(0), 1, 1, 1, 1	+4	0.054	0.056 ± 0.002	0.061 ± 0.006
(0), 1, 2, 1		0.055		
(0), 1, 1, 2		0.056		
(0), 1, 3		0.060		
(0), 2, 1, 1		0.054		
(0), 2, 2		0.057		
(0), 3, 1		0.060		
(0), 4		0.065		
(1), 1, 1, 1		0.054		
(1), 1, 2		0.056		
(1), 2, 1		0.056		
(1), 3		0.057		
(2), 1, 1		0.054		
(2), 2		0.056		
(3), 1		0.055		

correlation can also be represented as a linear dependence

$$\ln\rho = a - m\ln R_i, \quad (4)$$

(the a and m parameters are in Table 6). The expansion of this equation gives the expression

$$R_a^3 = bR_i^m + R_i^3. \quad (5)$$

However, since the ionic radii were determined less reliably than the atomic radii (the error of determination of a radius by Eq. (5) is larger than by Eq. (3), which is reflected in the root-mean-square deviation presented for both equations in Tables 5 and 6), the parameters of Eq. (5) are presented in Table 10 only for $n = 1$ and 2. For the other n values, the scatter of data is very large so that a reliable linear relationship cannot be obtained. Even for the n values used, the calculated radius value was introduced into the table only if the difference between this value and the experimental one for the atoms of a given element was no more than 10%.

An example of calculations of radii by Eq. (3) is presented in Table 7 (calculation by Eq. (5) is analogous). The first column specifies the valence states for which calculation was performed: 0 denotes a neutral atom, 1 corresponds to a singly charged positive ion (calculation by Eq. (3) at $n = 1$), 2 corresponds to a doubly charged positive ion (calculation by Eq. (3) at $n = 2$), etc. As follows from Table 7, calculations by different schemes give rather close values. A somewhat larger deviation was observed for calculations at $n = 3$ and $n = 4$; however, only the values that differed from the average value by three standard deviations were discarded from statistical processing. Table 3 shows as an

Table 8. Experimental and calculated average crystallographic radii of Period 4 elements for CN = 6

Element	Valence state	Radius, nm			
		average experimental radius	calculated radius		overall average radius
			by Eq. (3)	by Eq. (5)	
K	0	0.234	–	–	0.234
	+1	0.132 ± 0.004	0.132	–	0.132 ± 0.004
Ca	0	0.197	–	0.186	0.197
	+1	–	0.125	0.136	0.130 ± 0.005
	+2	0.100 ± 0.003	0.087 ± 0.0060	–	0.100 ± 0.003
Sc	0	0.164	–	0.183	0.164
	+1	–	0.112	0.128 ± 0.002	0.120 ± 0.012
	+2	–	0.084 ± 0.005	0.096	0.086 ± 0.005
	+3	0.076 ± 0.003	0.071 ± 0.006	–	0.076 ± 0.003
Ti	0	0.145	–	0.140 ± 0.003	0.145
	+1	–	0.103	0.104 ± 0.002	0.104 ± 0.002
	+2	0.080 ± 0.006	0.080 ± 0.001	0.081 ± 0.002	0.080 ± 0.006
	+3	0.066 ± 0.003	0.067 ± 0.004	0.065	0.066 ± 0.003
	+4	0.062 ± 0.003	0.055 ± 0.002	–	0.062 ± 0.003
V	0	0.135	–	0.142 ± 0.005	0.135
	+1	–	0.098	0.096 ± 0.003	0.097 ± 0.003
	+2	0.074 ± 0.006	0.078 ± 0.001	0.076 ± 0.006	0.074 ± 0.006
	+3	0.063 ± 0.003	0.065 ± 0.003	0.061	0.063 ± 0.003
	+4	0.058 ± 0.004	0.053 ± 0.004	–	0.058 ± 0.004
	+5	0.047 ± 0.010	0.046 ± 0.002	–	0.047 ± 0.010
Cr	0	0.128	–	0.128	0.128
	+1	–	0.094	0.095 ± 0.006	0.095 ± 0.006
	+2	0.080 ± 0.002	0.075 ± 0.002	0.075 ± 0.001	0.080 ± 0.002
	+3	0.061 ± 0.001	0.063 ± 0.002	0.061	0.061 ± 0.001
	+4	0.053 ± 0.006	0.054 ± 0.003	–	0.053 ± 0.006
	+5	0.049	0.045 ± 0.002	–	0.049
	+6	0.038 ± 0.010	0.040 ± 0.002	–	0.038 ± 0.010
Mn	0	0.130	–	0.145 ± 0.004	0.130
	+1	–	0.095	0.107	0.101 ± 0.006
	+2	0.083 ± 0.002	0.077 ± 0.003	–	0.083 ± 0.002
	+3	0.062 ± 0.002	0.065 ± 0.003	–	0.062 ± 0.002
	+4	0.050 ± 0.004	0.055 ± 0.003	–	0.050 ± 0.004
	+5	–	0.046 ± 0.002	–	0.046 ± 0.002
	+6	–	0.041 ± 0.002	–	0.041 ± 0.002
	+7	0.044 ± 0.002	0.036 ± 0.002	–	0.036 ± 0.008
Fe	0	0.127	–	0.127 ± 0.002	0.127
	+1	–	0.093	0.095 ± 0.001	0.094 ± 0.001
	+2	0.076 ± 0.002	0.075 ± 0.002	0.075	0.076 ± 0.002
	+3	0.062 ± 0.003	0.063 ± 0.002	–	0.062 ± 0.003
	+4	0.058	0.052 ± 0.003	–	0.052 ± 0.003
	+5	–	0.045 ± 0.002	–	0.045 ± 0.002
	+6	–	0.038 ± 0.002	–	0.039 ± 0.002
	+7	–	0.037 ± 0.003	–	0.037 ± 0.003
	+8	–	0.031 ± 0.003	–	0.031 ± 0.003

Table 9. Parameters of linear dependences of the square root of ionization potential on inverse ionic radius

	Period	*b*	*a*	σ^2
Ions with a noble-gas shell	3	3.48	0.361	0.27
	4	3.37	0.373	0.10
	5	0.84	0.635	0.24
	6	1.12	0.636	0.002
	7	0.71	0.712	0.03
Ions with a 10- and 18-electron shell	6	1.73	0.416	0.23
	5	–3.10	0.649	0.11
	6	–3.74	1.01	0.07
s, *p*, *d* Elements	4	–0.374	0.450	0.17
	5	–2.85	0.747	0.25
	6	–0.243	0.548	0.07
f Elements	6	–3.39	0.929	0.11
	7	–1.62	0.723	0.22

example the ionic radii calculated by Eqs. (3) and (5) for all valence states of a given Period 4 atom (the calculated ionic radii of unstable valence states are italicized). It is worth noting that Eqs. (3) and (5) have a broad flattened maximum in the radius range 2.0–3.0 nm; therefore, calculation of large radii, for example, for halide anions, gives values strongly different from the experimental values and, thus, unreliable ones. For this reason, the radii of anions were not determined, although these radii were calculated in [44].

As follows from Table 8, calculation by Eqs. (3) and (5) makes it possible to obtain close values. Equation (3) allows one to calculate a larger number of variants of high valence states (one value is obtained for a singly charged ion), whereas Eq. (5) gives a larger number of variants for the radii of low valence states. We can state that, for stable valence states, the calculated radii are consistent within the errors of determination. Comparison of the computational results [44] and [20], [43], and [45] for the known valence states with average crystallographic radii showed that our calculation by Eq. (3) provides coincidence within 6% and the calculation by Eq. (5), within 4%. The data in [44] and [43] are consistent within 11% and the data on [20], within 9%. The data in [45] cannot be compared since the authors used the table of radii [9] rather than calculated the radii of stable valence states.

Checking calculation values of average crystallographic radii for the known valence states coincided within the error of the experiment (0.004–0.006 nm) with the experimental average crystallographic radii (only the radii for which the error of determination was known, i.e., determined by several researchers, were used in calculations; the radii determined in a single work were not considered). The agreement between the calculated and experimental radii of atoms in stable valence states allows us to believe that the ionic radii of unstable valence states follow the general pattern.

Table 3 presents the average crystallographic radii of ions of the Period 4–7 elements calculated by Eqs. (3) and (5). Thus, the radii presented in Tables 2 and 3 constitute a nearly complete table of possible ionic radii, except for periods 2 and 3, for which the ionic radii of atoms in unstable valence states were not determined. Hereinafter, we use the values of the average crystallographic radii from Tables 2 and 3.

How are the ionic radii related to the parameters of atoms and ions? Let us consider two relationships.

The first relationship is that between the ionic radii of the same element. Inasmuch as the radii of a given element in different valence states are related to each other by equations like Eq. (2), the ratio of radii in various valence states must form one smooth curve for all elements of a given period. Figure 1 shows, as an example, the R_1/R_0, R_2/R_0, and R_3/R_0 ratios (the valence of the first ion is larger than the valence of the second ion by one, two, or three units; the second particle can be both the atom and the ion) as a function of the radius R_0 of the neutral atom or the ion in the lowest valence state. As is seen, the values for each n fall on the same curve for atom–ion and ion–ion pairs. This type of dependence can be used, if necessary, for minimizing average crystallographic ionic radii.

The second relationship pertains to ionization potentials. According to [6, 7], in isoelectronic series, the radius of an atom or ion is related to the nucleus charge by a simple equation

$$R = K/(Z - S),$$

where K is a constant, Z is the nucleus charge, and S is the shielding constant (smaller than unity), Therefore, the inverse ionic radius is proportional to the nucleus charge: $1/R$ is proportional to Z (within a period, the shielding constant retains its value and almost does not distort the plot in linear coordinates since it is small as compared with Z). Figure 2 shows the dependence of the inverse radius on the nucleus charge Z for all valence states of the Period 6 elements. As is seen, in isoelectronic series, the points for all groups of ions fall on straight lines with the same slope within the error of determination of a radius (to elucidate the accuracy, the errors of determination of each radius of the this series of ions are shown on the leftmost curve). The radii of unstable valence states (open circles) and the radii of stable valence states (solid circles) fall on the common line, which confirms, by and large, the correctness of the calculation of crystallographic ionic radii of unstable valence states. Analogous dependences are valid for the ions of Period 4, 5, and 7 elements. The correlation between the inverse radius and nucleus charge can also be used, if necessary, for refining the average crystallographic radii.

There is yet another, even more interesting, dependence. It was shown in [48] that there is a correlation

between ionization potentials and ionic radii. In [47], ionic radii as a function of ionization potential were calculated by the equation

$$r = \text{const}/I^2.$$

In [20], an additional coordinate ξ equal to the sum of the inverse numbers of electrons in separate electronic shells of ions was introduced for correlating the ionization potential with the ionic radius. This coordinate was used for calculating the radii of ions in unstable valence states. Figure 3 also points to the existence of a correlation between the ionization potential and ionic radius since, according to Moseley's law, the nucleus charge is related to the ionization potential as follows [54]:

$$(\nu/R_c)^{1/2} = (Z - S_n)/n,$$

where ν is the frequency of the characteristic X-rays emitted by an atom; R_c is the Rydberg constant; S_n is the shielding constant, which takes into account the influence of other electrons; and n is the principal quantum number. The left-hand term of this equation corresponds to the ionization potential. The nucleus charge is proportional to the inverse ionic radius; therefore, the above equations can be rearranged as follows:

$$I^{1/2} = 1/nR - S_n/n = a/R - b. \quad (6)$$

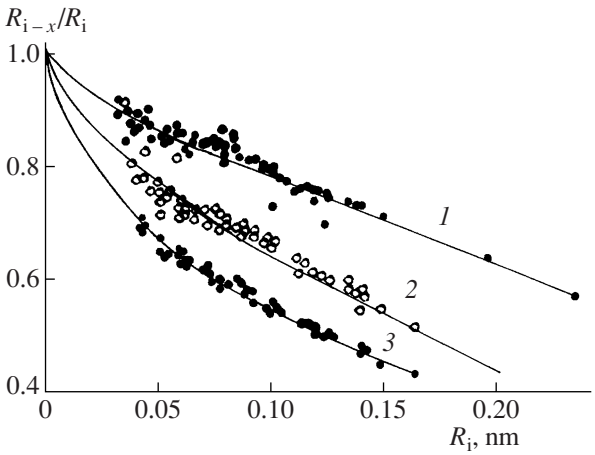

Fig. 1. Ratio of the radius of an ion in the lowest valence state to the radius of the second ion in the pair vs. R_i, nm for the charge difference of (*1*) one (*2*) two, and (*3*) three for Period 4 elements.

Table 10. Calculated ionization potential not presented in [55, 56]

Element	Valence state	*I*, eV	Element	Valence state	*I*, eV	Element	Valence state	*I*, eV
Pr	+4	51.4	At	+2	14.9	Pu	+7	70.9
Nd	+4	56.8	At	+3	22.9	Am	+	11.6
Pm	+4	56.8	At	+4	32.6	Am	+2	19.0
Sm	+4	58.8	At	+5	43.6	Am	+3	34.0
Eu	+4	53.1	At	+6	59.3	Am	+4	38.9
Gd	+4	58.8	At	+7	218	Am	+5	51.8
Tb	+4	65.3	Ac	+	15.9	Am	+6	62.3
Dy	+4	65.3	Pa	+	13.1	Am	+7	70.9
Ho	+4	67.3	Pa	+2	20.8	Cm	+	14.6
Er	+4	67.6	Pa	+3	28.4	Cm	+2	22.3
Tm	+4	65.3	Pa	+4	40.0	Cm	+3	33.1
Yt	+4	60.3	U	+4	42.3	Cm	+4	42.3
Lu	+3	33.4	U	+5	51.7	Cm	+5	55.0
Lu	+4	60.9	Np	+	14.2	Cm	+6	64.3
Hf	+4	47.3	Np	+2	24.5	Bk	+	17.3
W	+6	81.8	Np	+4	42.3	Bk	+3	33.1
Re	+7	101.9	Np	+5	49.0	Bk	+4	42.3
Os	+8	206	Np	+6	62.3	Bk	+5	55.0
Po	+	10.5	Np	+7	115.4	Bk	+6	64.3
Po	+2	17.8	Pu	+	15.9	Cf	+	18.1
Po	+3	25.3	Pu	+2	21.8	Cf	+2	29.9
Po	+4	35.1	Pu	+3	31.5	Cf	+3	35.9
Po	+5	44.8	Pu	+4	43.5	Cf	+4	50.3
Po	+6	172	Pu	+5	51.8	Cf	+5	56.7
At	+	8.9	Pu	+6	62.3	Cf	+6	64.3

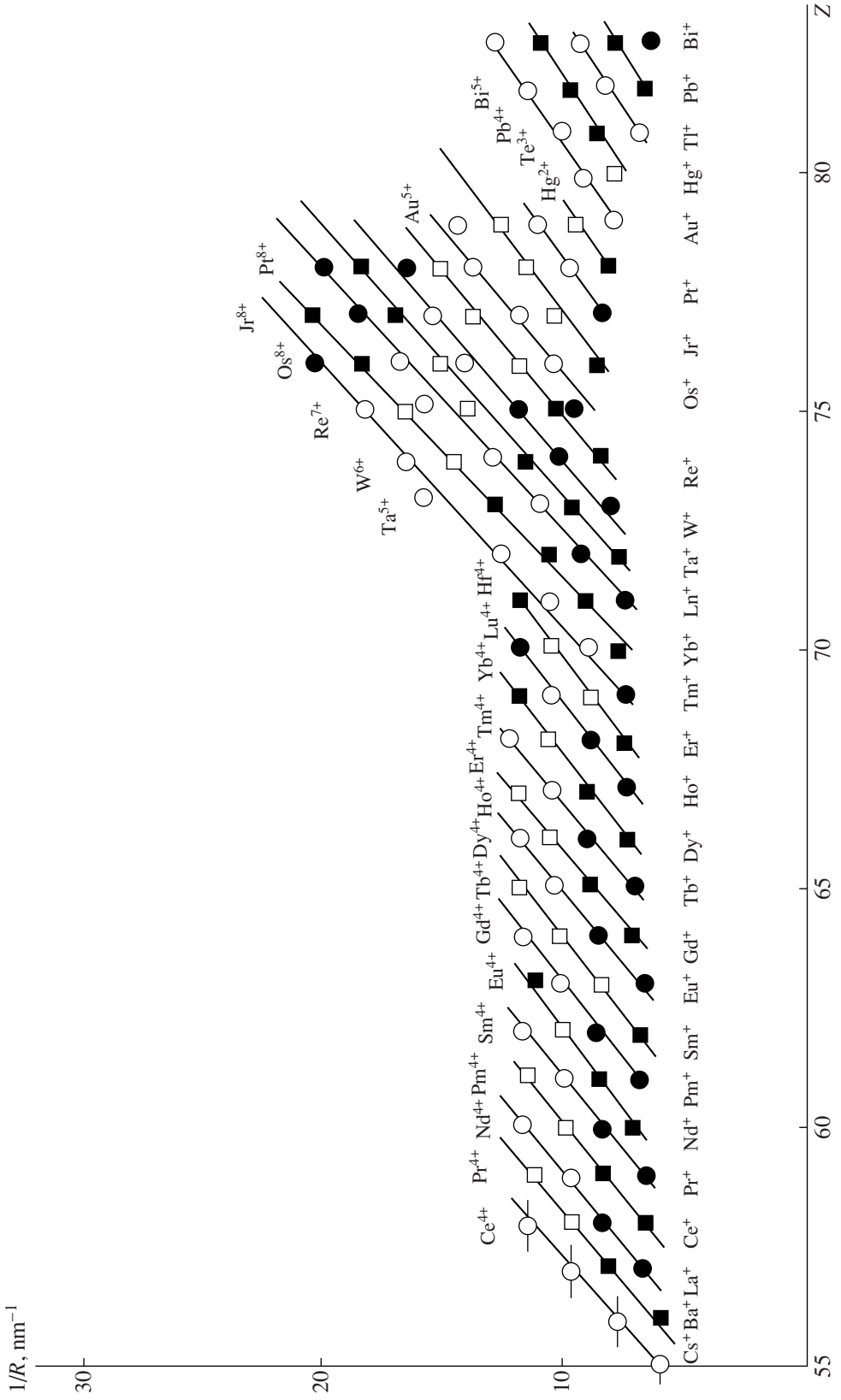

Fig. 2. Inverse ionic radius vs. nucleus charge for the Period 6 elements (open symbols are stable valence states, solid symbols are unstable valence states).

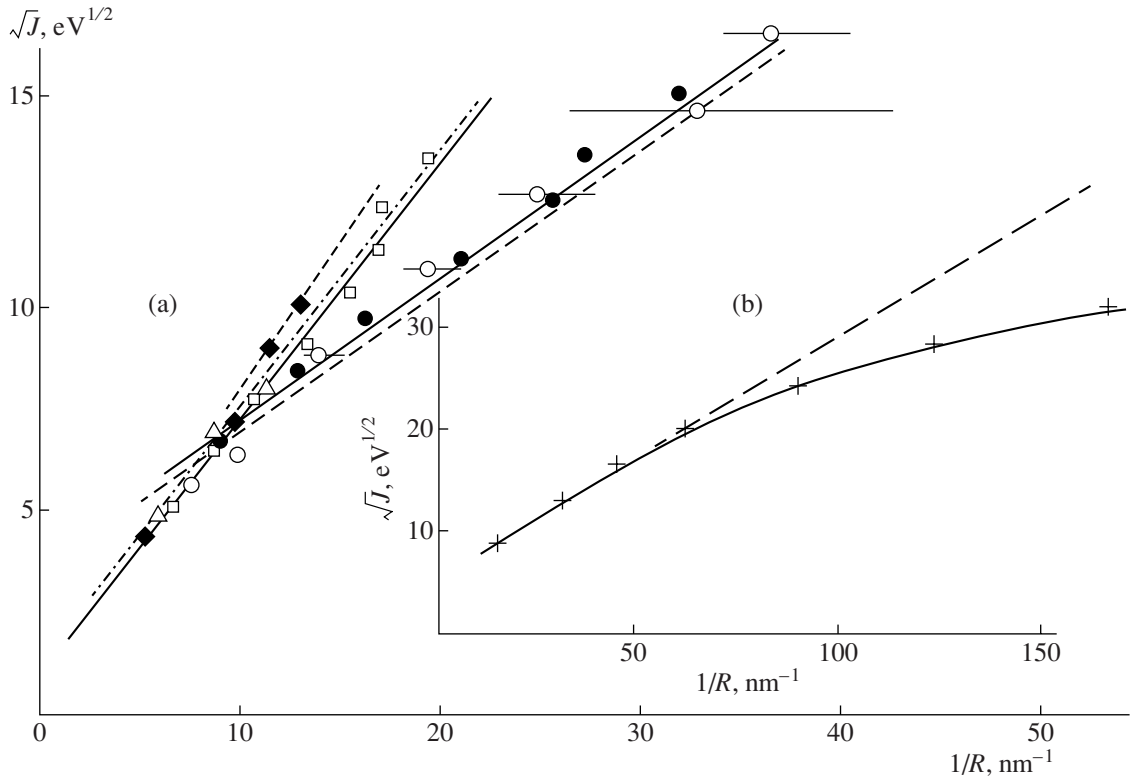

Fig. 3. Square root of ionization potential vs. inverse radius of an ion with a noble gas shell for (a) Period 3–7 elements and (b) (inset) for Period 2 (+) elements.

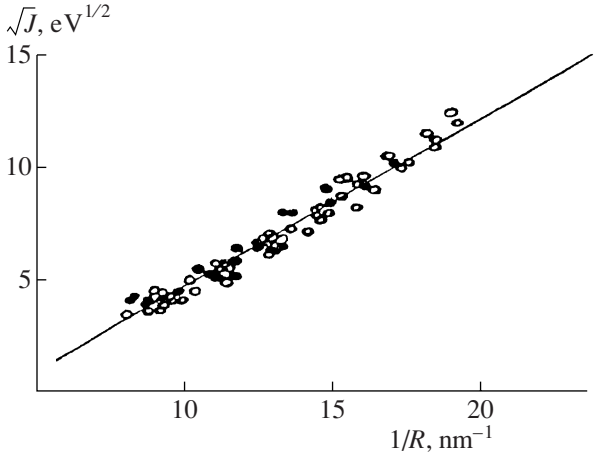

Fig. 4. Square root of ionization potential vs. inverse ionic radius for the Period 4 elements (open symbols are stable valence states, solid symbols are unstable valence states).

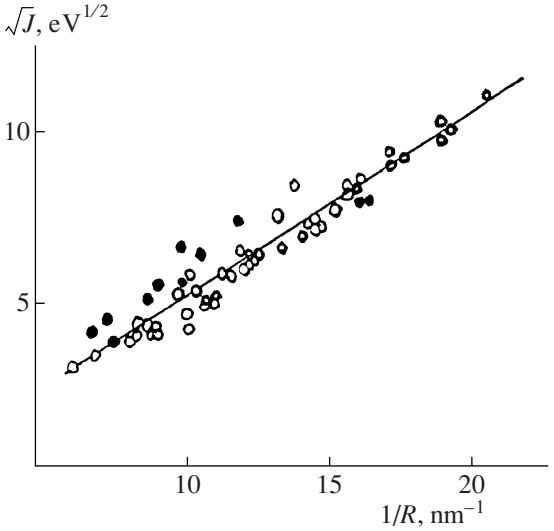

Fig. 5. Square root of ionization potential vs. inverse ionic radius for the Period 5 elements (open symbols are stable valence states, solid symbols are unstable valence states).

We obtain a simple equation that can easily be compared with the experiment. As dictated by the rules of filling of electronic shells [54], let us divide all ions into several groups: ions with a noble-gas shell; ions with an 18-electron shell; and the other ions, which we divide into the group of *s*, *p*, and *d* elements and the group of *f* elements. Figures 4–7 show the plots of the square root of the ionization potential versus the inverse ionic radius of a given ion for different groups of ions. The ionization potentials were taken from [55, 56].

Figure 4 shows the plots for isoelectronic groups of Period 2–7 ions with the shell of a preceding noble gas.

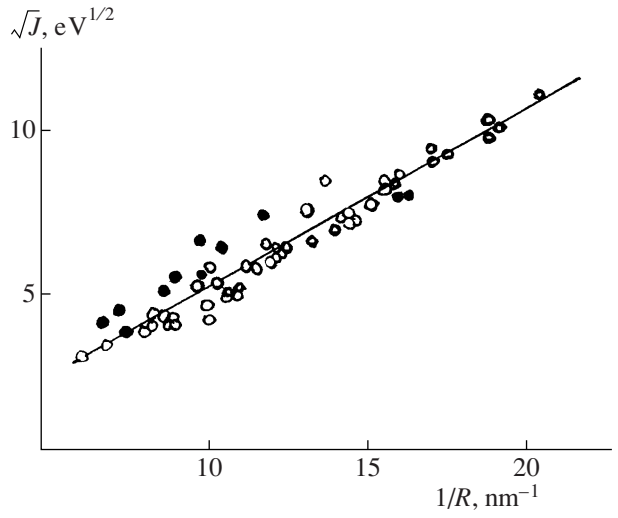

Fig. 6. Square root of ionization potential vs. inverse ionic radius for the Period 6 elements (open symbols are stable valence states, solid symbols are unstable valence states).

As is seen, all the plots are straight lines forming two subsystems: 3–4 and 5–7. In each subsystem, the coefficients of Eq. (6) are close. For Period 2, Eq. (6) is not valid (it cannot be ruled out that the ionic radii of nonmetal elements are underestimated). The coefficients of Eq. (6) for these and next groups of ions are presented in Table 9. For the isoelectronic series of ions with a filled 18-electron shell, Eq. (6) is valid but has other coefficients.

Figures 4–6 show the plots of the square root of the ionization potential versus the inverse radius of *s*, *p*, and *d* elements for the ions not belonging to the first two groups. As can be seen, the square roots of the ionization potentials satisfactorily fit the linear plot versus the inverse ionic radius for all ions not belonging to the first two groups. It is strange that this fact escaped the attention of the previous researchers. It is likely due to a different operation used for determining the radii of ions in unstable valence states. These values do not fall on straight lines; therefore, only second and higher ionization potentials were used. It is worth noting that the data on stable valence states (solid symbols) are almost the same as the data on unstable states (open symbols). Naturally, the question arises as to what ionization potential value is in the solid state. We believe that the used gas-phase ionization potentials, second and higher ones, change slightly when these elements transform into a solid so that this change is hardly perceptible against the background of the error of determination of ionic radii of several percents. It is evident that some change should occur since the electron binding energy changes by a fraction of a percent even in going from a free atom to the atom in a molecule, which is demonstrated by X-ray photoelectron spectroscopy.

Figure 7 shows the data for the Period 6 and 7 *f* elements. As is seen, Eq. (6) is also valid for these elements, but it has other parameters as compared with those for the *s*, *p*, and *d* elements (Table 9).

The resulting values of parameters (Table 9) make it possible to calculate the as yet unknown ionization potentials. The results of such calculations for 78 ions are summarized in Table 10.

Thus, the complete table of ionic radii allows us to determine not only the crystal-chemical parameters but also the properties of the atoms (i.e., ionization potentials). In essence, the ionic radius is the distance of an electron in the orbital from the center of the atom, i.e., the characteristic corresponding to the planetary model of the atom. In our opinion, the average crystallographic radii should be a routin characteristic of all ions.

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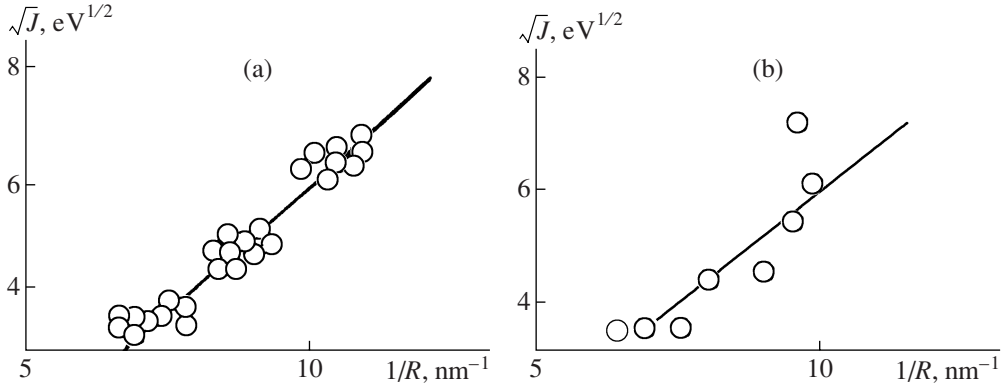

Fig. 7. Square root of ionization potential vs. inverse ionic radius for the *f* elements of Periods (a) 6 and (b) 7.

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