The Journal of the American Chemical Society

VOL. 50 NOVEMBER, 1928 No. 11

[Contribution from the Chemical Laboratory of The Johns Hopkins University]

STUDIES ON THE PERIODIC SYSTEM.
I. THE IONIC POTENTIAL AS A PERIODIC FUNCTION[1]

By G. H. Cartledge

Received April 7, 1928 Published November 6, 1928

In the more recent modifications of the periodic system emphasis has been placed upon the structure of the elements as the basis of classification. All forms of classification, however, suffer from the same essential difficulty, namely, that the elements have too protean a nature to be adequately classified by reference to any single atomic characteristic. For chemical use it is highly desirable that a periodic arrangement be devised which shall be based upon a more comprehensive and quantitative view of the elements and shall also provide a place for all valence forms of all elements. It is one of the serious defects of the Mendelejeff system that it has no quantitative basis, so that it is unable to indicate gradations in properties within a series or a family.

While the comparison of atomic structures gives a partial indication of variations in chemical behavior, even this is not adequate, inasmuch as the properties of *compounds* are to an important extent determined by the sizes of their ionic constituents as well as by their structures. The role of the ionic radii has been emphasized by Grimm,[2] and by v. Hevesy.[3] Grimm has also given a periodic classification in which the direction of variation in radii is represented.[4] The importance of certain electronic structures in giving different valence forms of the same element has been shown by Grimm and Sommerfeld.[5]

In order to obtain a more comprehensive representation of the properties of compounds, it is proposed in this paper to take account of the *charge, structure* and *size* of the ionic constituents of compounds, and to develop a form of representation in which it will be possible to include all valence forms of all of the elements. As a consequence of this broader and quanti-

---

[1] In memory of Ira Remsen.

[2] Grimm, *Z. physik. Chem.*, **98**, 353 (1921); *ibid.*, **102**, 113, 141 (1922).

[3] G. v. Hevesy, *Z. anorg. allgem. Chem.*, **147**, 217 (1925).

[4] Grimm, *Z. physik. Chem.*, **101**, 410 (1922).

[5] Grimm and Sommerfeld, *Z. Physik*, **36**, 36 (1926).

tative basis of classification, the new arrangement eliminates the earlier difficulties with respect to the classification of hydrogen, the properties of the rare earths, the higher valence forms of copper, silver and gold, and the relations of the eighth-group elements. Being based upon ions rather than atoms it gives a clearer representation of the chemical relationships.

The Ionic Potential

In determining the properties of substances, increasing ionic charge and increasing ionic radius act in opposite directions; thus, the lattice energy of a binary polar crystal is chiefly determined by the Coulomb term, $Z^2e^2/(r_+ + r_-)$, in which e is the electronic charge and Z and r are, respectively, the valence and radius of the ions. In the same way, oxides are increasingly acidic the higher the charge or, for constant charge, the smaller the radius of the positive ion. This consideration suggests that the ratio of charge to radius should be an important property of ions and closely related to many characteristics of substances. If the ion in a crystal is regarded as a charged sphere of definite extension in space, this function is the *ionic potential* and will be represented by ϕ; that is, $\phi = Z/r$. Of course the ion in a crystal is not a conducting sphere in the strict sense, so that in calling this function the ionic potential we are using a somewhat hypothetical concept as a basis of classification. Ions actually have a real charge and a real extension in space, however, and these characteristics are observed to have a determining influence upon the properties of their compounds, so that the ratio of charge to radius is a real property of the ion.[6]

In this method of treatment it is not necessary to assume the free existence as ions of such substances as S^{6+} or C^{4-}. In crystals such as sodium chloride the lattice is undoubtedly ionic, while the intra-ionic bonds in sulfate ions, for instance, are generally regarded as non-polar. Since ions of the same structure have radii which are inversely proportional to the effective nuclear charge, the radius may be found for the electrical system corresponding to S^{6+}, even though this may not exist as a separate entity. It is only in this sense that S^{6+} will be called an ion. If it is a transition from polar to non-polar binding which is associated with the variation in properties in going through a periodic series, then it appears that this transition is directly related to the magnitude of the ionic potential, which therefore becomes an index of properties, even though calculated for hypothetical ions such as S^{6+}.

Ionic radii have been calculated from crystal data by Grimm and

---

[6] Another similar function might be used, namely, the electrostatic energy of the ion, $Z^2e^2/2r$. This possibility has been investigated, and a classification results similar to the one here given. The simpler function is to be preferred, however, in most cases.

Wolff[7] and, more recently, on the basis of the wave mechanics, by Pauling.[8] The data of Pauling have been used, as far as they go, in calculating the ionic potentials. For this purpose the ionic charge Z corresponding to the valence is divided by the radius in Ångström units. These arbitrary units of potential are sufficient to indicate the comparisons desired.

In order to obtain ionic potentials for all the elements it is necessary to use indirect methods in certain instances. The available data on the radii have been extended in the following manner.

(a) The ionic potential is directly related to the ionization potential for the removal of the *last* electron in the production of the ion in question. As was found by Millikan and Bowen,[9] there is a linear relation between the atomic number and the square root of the energy corresponding to the removal of the electron in a series of ions of the same structure. This is an extension of the Moseley rule for x-ray frequencies into the region of optical spectra. Correspondingly, for positive ions it is found that *the square root of the ionic potential increases in very approximately equal steps as the ionic charge increases without alteration in structure.* For this reason the square root of the potential is given in some of the graphs and tables which follow, and unknown potentials may be very closely estimated by this *method of constant increments.* The increment $\Delta\sqrt{\phi}$ becomes less as the principal quantum number of the outermost electrons in the ion increases. This method has been used in finding values for Ta^{5+}, W^{6+}, (75^{7+}) and Os^{8+}, the calculations being based on the potentials for Lu^{3+} and Hf^{4+}, as found in the way described in (c) below; for Po^{6+} and (85^{7+}) by reference to Bi^{5+}; and for the series Ra^{++} to U^{6+} by reference to Ra^{++} and Th^{4+}.

(b) Within the alkali and alkaline earth families there is a linear relation between the ionization potential and the square root of the ionic potential, from the sodium to cesium series, inclusive. From this relation and the known ionization potential of radium, the value of $\sqrt{\phi}$ for radium is found to be 1.24. This value, combined with that for thorium (1.90), gives the increment in $\sqrt{\phi}$ as 0.33 for unit change in charge in the series Ra^{++} to U^{6+}.

(c) Radii for the rare earth ions were computed by Grimm and Wolff[7] from the lattice spacing of the oxides as given by Goldschmidt.[10] These measurements show that the ionic radius decreases from lanthanum to lutecium, the jump being apparently larger from La^{3+} to Ce^{3+} than it is elsewhere in the series. In order that all of the radii used in estimating potentials may be consistent with each other, the radius of Lu^{3+} has been calculated from that of Y^{3+} as given by Pauling by taking the lengths of the unit cells in the cubic forms of Y_2O_3 and Lu_2O_3 as 10.60 Å. and 10.37 Å., respectively. This gives 0.88 Å. as the radius of Lu^{3+}, corresponding to $\sqrt{\phi} = 1.85$. Values for the other rare earths have been interpolated, following the data of Grimm and Wolff.

Since the external structures are alike in the series Cs^{+} to Ce^{4+} and Hf^{4+} to Os^{8+}, and since these ions belong to the same periodic series, it is reasonable to assume that the increment in $\sqrt{\phi}$ per group is the same in both parts of the series. The value 0.40 as obtained from Ba^{++} and Ce^{4+} is used for $\Delta\sqrt{\phi}$ in estimating the potentials from Lu^{3+} to Os^{8+}.

---

[7] Grimm and Wolff, *Z. physik. Chem.*, **119**, 254 (1926); Grimm, *ibid.*, **122**, 177 (1926).

[8] Pauling, This Journal, **49**, 765 (1927).

[9] Millikan and Bowen, *Phil. Mag.*, [7] **4**, 561 (1927).

[10] Goldschmidt, *Skrifter Norske Videnskapsakad. Oslo, I, Matemat.-natur. Klasse,* **1926**, No. 2.

(d) The potential of the hydrogen ion H^+ can be estimated only indirectly and approximately, owing to the unique character of the ion in all respects. As will be pointed out subsequently, the heat of hydration of the gaseous ion is related to the ionic potential. There is a linear relation for the alkali ions, and if this is used in connection with the heat of hydration of the H^+ ion, it gives a value of about 2 for $\sqrt{\phi_{H^+}}$. The ionization potential of the alkali elements also varies in the same order as the ionic potential, and extension of the curve indicates an ionic potential for H^+ corresponding to $\sqrt{\phi} = 4$ approximately. On account of the unique structure of the hydrogen ion it is hardly to be expected that any single constant can be obtained which will be a quantitative indication of all the properties of its compounds; this divergence in the values is not surprising, therefore, since they correspond to very different types of behavior. Nevertheless, as will be seen below and in the subsequent paper, a mean of the values obtained above serves to indicate properly the general relation of hydrogen compounds, such as hydrogen chloride and water.

Table I gives the square root of the ionic potentials obtained in the ways just described. The values are in arbitrary units, the charge being taken as the valence and the radius being expressed in Ångström units. A negative sign is attached to the values for the anion potentials. No attempt has been made to estimate potentials for ions which have an electron pair in the ion, such as Ge^{++}. Aside from the paucity of data for such cases, there is the further complication that tautomerism is apparently a common phenomenon in such valence forms, for example,

TABLE I

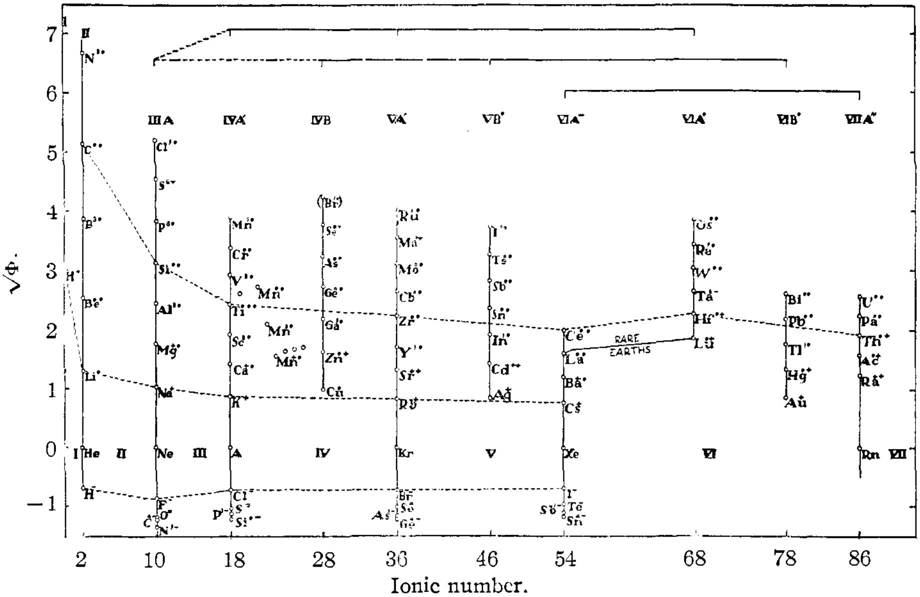
SQUARE ROOT OF IONIC POTENTIALS (ARBITRARY UNITS)

				H^+							
				3							
			H^-	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	(O^{6+})	(F^{7+})	
			−0.69	1.29	2.54	3.87	5.16	6.71	(8.19)	(10)	
C^{4-}	N^{3-}	$O^{=}$	F^-	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	
−1.24	−1.32	−1.19	−0.86	1.02	1.76	2.45	3.13	3.83	4.55	5.20	
$Si^{4}{}_{-}$	P^{3-}	$S^{=}$	Cl^-	K^+	Ca^{++}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}	
−1.22	−1.19	−1.04	−0.74	0.87	1.42	1.92	2.43	2.92	3.39	3.90	
				Cu^+	Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	(Br^{7+})	
				1.02	1.64	2.20	2.74	3.26	3.78	(4.24)	
Ge^{4-}	As^{3-}	$Se^{=}$	Br^-	Rb^+	Sr^{++}	Y^{3+}	Zr^{4+}	Cb^{5+}	Mo^{6+}	Ma^{7+}	Ru^{8+}
−1.21	−1.16	−1.00	−0.715	0.82	1.33	1.79	2.24	2.66	3.11	3.56	4.01
				Ag^+	Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}	
				0.89	1.44	1.92	2.36	2.84	3.27	3.74	
Sn^{4-}	Sb^{3-}	$Te^{=}$	I^-	Cs^+	Ba^{++}	La^{3+}	Ce^{4+}				
−1.17	−1.10	−0.95	−0.68	0.77	1.21	1.61	2.00				
						Lu^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+}	Os^{8+}
						1.85	2.25	2.65	3.05	(3.45)	3.85
				Au^+	Hg^{++}	Tl^{3+}	Pb^{4+}	Bi^{5+}	Po^{6+}	85	
				0.85	1.35	1.78	2.18	2.60	3.02		
				87	Ra^{++}	Ac^{3+}	Th^{4+}	Pa^{5+}	U^{6+}		
					1.24	1.57	1.90	2.23	2.56		

$Ge(OH)_2 \rightleftarrows HGeOOH$, sulfurous acid, and others, so that the electrical system is not well defined.

Radii are known for some of the transition ions, so that their ionic potentials may be found. During the completion of an 8-shell, as from Ca^{++} to Zn^{++}, there is a distinct contraction as the first electrons are added, so that the transition ion has a higher potential than the equivalent ion with the inert-gas structure: $\phi_{Mn^{++}} > \phi_{Ca^{++}}$. The data are inadequate to permit tracing the variation during the complete transition from Ca^{++} to Zn^{++} or from Sc^{3+} to Ga^{3+}, for example, but the trend is indicated by the following values, some of which are included in Fig. 1.

Ion	Ca^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Ti^{4+}	V^{4+}	Mn^{4+}	Zr^{4+}	Cb^{4+}	Mo^{4+}	Ru^{4+}
$\sqrt{\phi}$	1.42	1.57	1.64	1.67	1.70	2.43	2.61	2.72	2.24	2.44	2.46	2.52



Electron shells	K	2	2	2	2	2	2	2	2	2	2
	L		→ 8	8	8	8	8	8	8	8	8
	M			→ 8	→ 18	18	18	18	18	18	18
	N					→ 8	→ 18	18	→ 32	32	32
	O							→ 8	8	→ 18	18
	P										→ 8

Fig. 1.—Square root of the ionic potentials.

Ionic Potentials and the Periodic System

There are obviously three characteristics of the ions that should be represented in the periodic system, namely, the electronic structure, the net charge and the ionic potential. For simplicity we shall define the *ionic number* as the number of extra-nuclear electrons in the *ion*, corresponding to the *atomic number* for atoms. For graphical representation the square root of the ionic potential is plotted against the ionic number in Fig. 1. A still clearer representation is given by a three-dimensional model, a photograph of which is shown in Fig. 2. In this the ionic number and ionic charge are the axes in the plane of the board, while the height of the rods is proportional to $\sqrt{\phi}$ (omitting the negative sign of the anion potentials).

These arrangements emphasize the predominance of certain ionic structures, as was suggested in Kossel's diagram.[11] The periods also are clearly shown in accordance with the requirements of the Bohr theory, the periods being designated by a number equal to $n + 1$, in which n is the quantum number of the outer electrons in the ion.[12] While by no means all known valence forms of the elements are shown in Fig. 1, holes have been drilled in the board in the model for all of them, and the potential of any ion may be estimated by considering the general order of variation. In Figs. 1 and 2 several valence forms of manganese are shown in order to illustrate the principle.

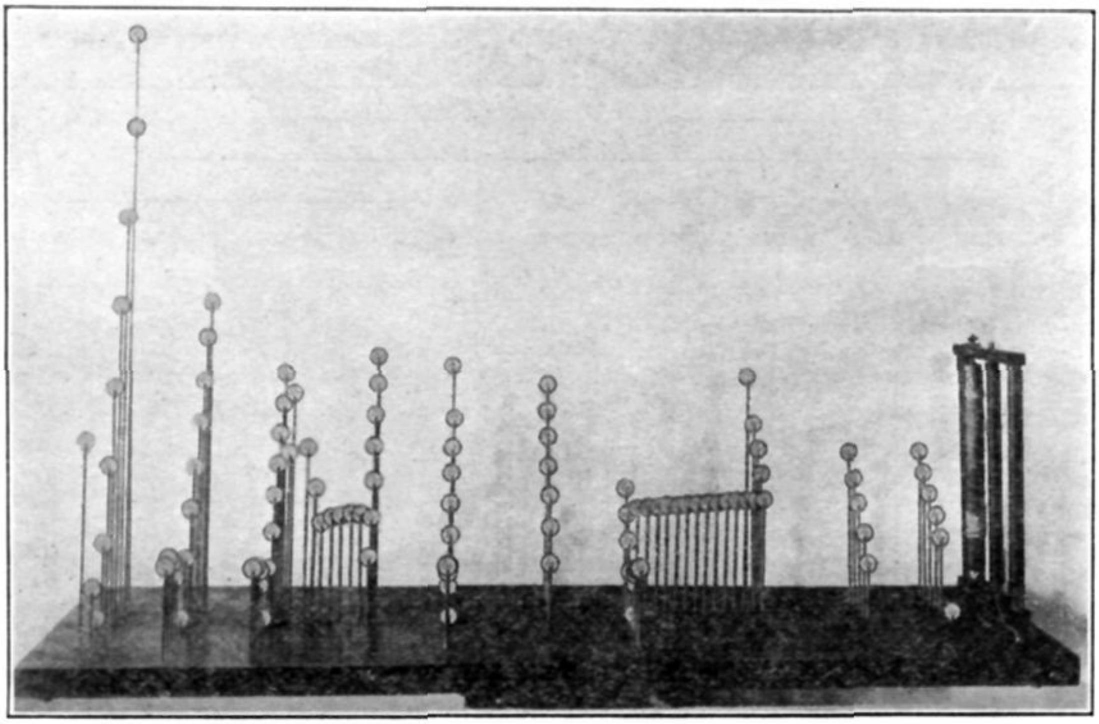


Fig. 2.—Model of the periodic system of ions. From left to right, ionic numbers; front to back, ionic charges ($^{4-}$ in front to $^{8+}$ at back); height of rods gives $\sqrt{\Phi}$.

The rapid variation in properties in the series Li^+ to N^{5+} is revealed

---

[11] Kossel, *Ann. Physik*, **49**, 229 (1916).

[12] In this way *positive* ions that are fully oxidized belong to the ionic series of the same numerical designation as is used by Bohr for the series of elements. Partly reduced positive ions (Fe^{++}, P^{3+}) are given the same series number as the fully oxidized ions, while fully reduced anions, such as Cl^-, belong to the next higher ionic series.

by the large increment in $\sqrt{\phi}$. This makes these ions more or less unique in comparison with corresponding ions of the series below. The dual character of hydrogen in giving both an alkali-like ion H^+ and a halogen-like ion H^- is shown by its double location in the system. The numerical value of $\sqrt{\phi_{H^+}}$ shows, however, that H^+ resembles the alkali ions only in valence, its potential placing it along with Si^{4+} and Ti^{4+}, while H^- is quite like a halide ion in general relations. Correspondingly, liquid HCl and $SiCl_4$ are volatile, non-conducting substances, while LiCl and LiH are high-melting substances which conduct electrolytically in the fused state.

It is obvious that the eighth-group triads are provided for in a logical manner, as is also the case with Cu^{++}, Ag^{++} and Au^{3+}. The disposition of the rare earths is particularly significant. As will be pointed out subsequently, the basic properties of an ion diminish with increasing potential. Whereas there is, in general, an increase in basic character with increasing atomic weight in comparing ions of the same valence, this order is reversed in the rare earths, so that lutecium is even less basic than yttrium. These relations are accurately shown by the ionic potentials, and it is strikingly indicated that yttrium falls in the rare-earth elements in the neighborhood of dysprosium and holmium (which accords with its experimental behavior) while scandium is less basic (higher potential) than lutecium. The relation of the rare earths to the bivalent ions is shown in the near equality of the potentials of lanthanum and magnesium.

It will be convenient to speak of ions having very nearly equal potentials as *equipotes*.

The Periodic Families of Ions

Although it will be shown in the succeeding paper that the ionic potentials are a reliable index to the variation of numerous properties, it is necessary to remember that the ionic structure must also be taken into account in comparing the chemical and physical character of ions and their compounds. There is a close connection between the chemical relationships of the different families and series of ions and the character of their outer electronic shells, *particularly with respect to the completeness or incompleteness of these shells.* This observation has suggested a modification of the division into families as made by Mendelejeff. The successive shells are complete when they contain, respectively, 2, 8, 18, 32, and 50 (?) electrons, so that the *ionic types* to be distinguished on this basis are as shown in Table II.

In this representation *A* or *B* is used only if the simplest ion of the series has two or more electronic groups. *A* is used if the outer shell is either a simple 8-shell or a partial development of one, as $K^+ = 2,8,8$; $Mn^{7+} = 2,8,8$; $Mn^{++} = 2,8,13$. *B* is used for an outer shell of 18 or a

TABLE II

PERIODIC SERIES AND FAMILIES OF IONS

Series designation	Outer shell	Next underlying shell	Examples
I	0	..	H^+ only
II	2	..	H^-, N^{5+}
III *A*	8 (complete)	2 (complete)	C^{4-}, Cl^{7+}
IV *A′*	8 (incomplete)	8 (complete)	Si^{4-}, Mn^{7+}
IV *B*	18 (complete)	8 (complete)	Cu^+, Se^{6+}
V *A′*	8 (incomplete)	18 (complete)	Ge^{4-}, Ru^{8+}
V *B′*	18 (incomplete)	18 (complete)	Ag^+, I^{7+}
VI *A″*	8 (incomplete)	18 (incomplete)	Sn^{4-}, Ce^{4+}
VI *A′*	8 (incomplete)	32 (complete)	Lu^{3+}, Os^{8+}
VI *B′*	18 (incomplete)	32 (complete)	Au^+, Po^{6+}
VII *A″*	8 (incomplete)	18 (incomplete)	Ra^{++}, U^{6+}

development of one, as $As^{5+} = 2,8,18$; $As^{3+} = 2,8,18,2$. The prime marks are used to indicate the incompleteness of the two outer 8 or 18 shells; a single prime mark signifies that only the outer 8 or 18 shell is incomplete; a double prime denotes that the two outermost 8 or 18 shells are incomplete.

Inspection of Fig. 1 reveals the close relationships indicated by the brackets in the upper portion of the figure. This method of defining the periodic families brings out clearly the effects associated with the "lanthanide contraction,"[13] such as the association in nature of zirconium with hafnium, of columbium with tantalum, and so forth. The classification also serves to indicate the unique character of the ions of series I (H^+) and II ($Li^+ - N^{5+}$), as well as the double relationship of the ions of series III A, which are most like A′ members in the first two groups but more like B ions in groups III to VII.

This definition of the periodic families taken in connection with Fig. 1 serves to bring out the differences among the members of a given family in the Mendelejeff arrangement. In the alkali family, for example, the relatively large divergence in properties between lithium and sodium and also between sodium and potassium is clearly shown. Potassium and rubidium have very nearly equal potentials (and properties) while the differences between rubidium and cesium are somewhat larger (less marked isomorphism, for example). Even in Group IV, in which family differences are less pronounced than in other groups, the variations in properties are significantly shown. Titanium, zirconium and hafnium are thrown together, the last two having equal potentials and very similar properties, while cerium and thorium are in another family with somewhat different potentials. The near equality of the potentials of both A and B families in Group IV corresponds to the extensive isomorphism which occurs in many of their compounds.

---

[13] Goldschmidt, Barth and Lunde, *Skrifter Norske Videnskaps.-Akad. Oslo., I, Matemat. Natur. Klasse*, 1925, No. 7; v. Hevesy, *Z. anorg. allgem. Chem.*, **147**, 217 (1925).

The relation of the ionic potential to certain properties of compounds will be shown in subsequent papers, in which it will appear that the numerical values of the potentials may be used to indicate the order of variation of numerous effects.

Summary

1. A periodic classification of ions has been developed, with provision for all valence forms of all the elements. It is shown that no single atomic characteristic is an adequate basis for a periodic classification, and the new arrangement takes account of the charge, structure and radius of the ions. For this purpose a new function, the ionic potential, is introduced and used as a quantitative basis for the classification.

2. It is shown that the ionic potential is related to many of the characteristics of ions and their compounds, and that the new arrangement satisfactorily represents the behavior of hydrogen, the eighth group elements and the rare earths.

3. It is also shown that the properties of the ions are definitely related to the structure of their outermost electronic shells, with respect to the completeness or incompleteness of these shells. On this basis a new definition of the periodic families is given.

Baltimore, Maryland

[Contribution from the Chemical Laboratory of The Johns Hopkins University]

STUDIES ON THE PERIODIC SYSTEM. II. THE IONIC POTENTIAL AND RELATED PROPERTIES[1]

By G. H. Cartledge

Received April 7, 1928 Published November 6, 1928

In the preceding paper[2] it has been shown that the ratio of charge to radius is an important periodic property of the ions and may be made the basis of a quantitative classification. This function has been called the ionic potential. In the present paper the relation between the ionic potential and several related properties of substances will be developed, and it will be shown that the periodic classification presented in the preceding paper is able to indicate the order of variation of many properties which may not readily be related to the older forms of representation.

Ionic Hydration and Associated Effects

When a polar crystal is placed in water the lattice becomes disrupted under the influence of the attraction between the ions and the polarized water molecules. Following Fajans,[3] the measured heat of solution, Q_s,

---

[1] In memory of Ira Remsen.

[2] Cartledge, This Journal, **50**, 2855 (1928).

[3] Fajans, *Ber. physik. Ges.*, **20**, 712 (1918); *ibid.*, **21**, 549, 714 (1919).