Anomalous Behaviour of Elements 13 to 20 as Related to Atom Oversize

By JESSE ELSON

(*Department of Chemistry, Delaware Valley College, Doylestown, Pennsylvania* 18901)

Summary Certain physical and chemical properties of Al, Si, P, S, Cl, Ar, K, and Ca appear to be anomalous and are related to atom oversize.

THE elements Al, Si, P, S, Cl, and Ar have larger electron affinities (EA) and smaller ionization potentials (IP) than would be expected from number of electrons in each element. These oddities are evident when each element is compared with others in its respective group (Table 1) in a log–log plot of EA (and of IP) against total electrons in the atom.

A similar comparison of polarizabilities shows that the values for Cl^- and K^+ are about 50% larger than would be expected from the number of electrons in each ion. Atom polarizability values[1] are measurements on alkali halide crystals, while estimates of the polarizability of the free ions show the same trends.[2]

Similarly, thermodynamic data[3] show small values of absolute enthalpy of hydration for Cl^-, K^+, and Ca^{2+}, and a large value for Na^+. The same trend is evident for other absolute hydration data (entropies and free energies).

Solubility data[4] (molalities for saturated water solutions at 20°) show odd behaviour for K and Cl. The mean of the four halides of K is approximately equal to that of the larger Rb. Similarly, the mean of the five alkali-metal chlorides is equal to that of the five bromides.

Crystal density data show anomalous behaviour for S, Cl, K, and Ca. The chlorides have the smallest densities of the four halides of each of the following representative metal ions: alkali metals, alkaline-earth metals, Al^{III}, Ga^{III}, In^{III}, Tl^{III}, Pb^{II}, As^{III}, Sb^{III}, Bi^{III}, Cr^{II}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Ag^{I}, Zn^{II}, Cd^{II}, Hg^{I}, and Hg^{II}.

A similar comparison of the alkali-metal halides shows that the potassium salts have the smallest densities for each halogen, and that the value for KCl is the lowest for the 20 alkali-metal salts.

The sulphides have the smallest densities of the four chalcogenides of each of the following representative metal ions: alkali metals, alkaline-earth metals, Al^{III}, Ga^{III}, In^{III}, Pb^{II}, As^{III}, Sb^{III}, Bi^{III}, Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Cu^{I}.

A comparison of the densities of the alkaline-earth metal chalcogenides shows that CaS has the smallest value.

Other comparisons of alkali halides show Cl to act oddly. Plots of internuclear distance and of volume compressibility against Δb value of alkali-metal–halogen bond give large values for KCl, RbCl, and CsCl.[5]

Odd bonding behaviour is exhibited by elements in the third row of the Periodic Table, including phosphorus and sulphur, which are able to expand the valence shell beyond 8 electrons. The ability of sulphur to have 10 or 12 electrons in its valence shell is usually explained by its utilization of unoccupied 3*d*-orbitals.

TABLE 1

Groups of Elements

Group	Elements
0	He, Ne, Ar, Kr, Xe
I	Li, Na, K, Rb, Cs
II	Be, Mg, Ca, Sr, Ba
III	B, Al, Ga, In, Tl
IV	C, Si, Ge, Sn, Pb
V	N, P, As, Sb, Bi
VI	O, S, Se, Te
VII	F, Cl, Br, I

Atom Size and Number of Electrons.

The anomalies in physical and chemical properties of elements 13 to 20 correlate with atom oversize.

A log–log plot of elements in each Group (0—VII) between covalent radius and total electrons yields equation (1), which expresses atom size as a power function of number of electrons in the atom.

$$r = kE^s \quad (1)$$

where r is atom radius (Å), E is total electrons in atom, and k and s are constants for each Group as shown in Table 2.

TABLE 2

Constants for equation (1)[a]

Group	k (Å/electron)	s	Element	k' (Å/electron)	Element	k' (Å/electron)
0	0·80	0·22	Ne	0·79	Ar	0·92
I	1·10	0·18	Na	1·0	K	1·16
II	0·59	0·30	Mg	0·61	Ca	0·70
III	0·58	0·21	Al	0·68		
IV	0·50	0·25	Si	0·58		
V	0·44	0·27	P	0·51		
VI	0·37	0·33	S	0·41		
VII	0·34	0·34	Cl	0·37		

[a] Calculated for equation (1) from experimental data.

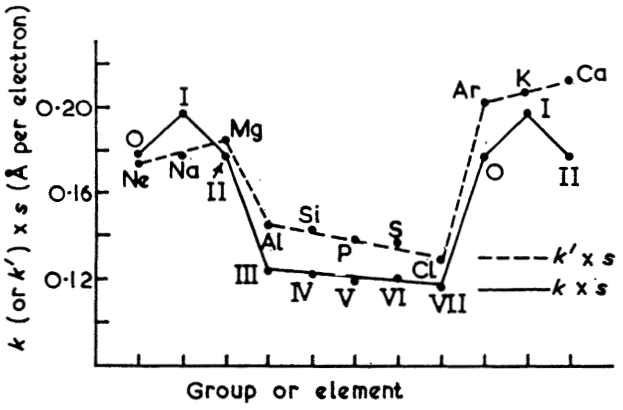

FIGURE. k (*or* k') × s *against group or element.*

Since the k and s values are constant, the product ks is likewise constant, and is shown for each Group in the Figure.

A k' value is calculated for each element with equation (1) using the respective Group value of s. The $k's$ values for elements 13 to 20 are larger than the respective Group values as seen in the Figure. The $k's$ values of the other elements (except Na) exhibit an insignificant spread from the respective ks values.

Since k' (or k) has the dimensions of Å per electron, elements 13 to 20 are oversized as judged by comparing them with others in their respective groups.

(*Received, April 8th,* 1969; *Com.* 496.)

[1] W. Shockley, *Phys. Rev.*, 1964, **70**, *A*, 105.
[2] M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," Oxford University Press, London, 1954, 1st edn., p. 107.
[3] R. M. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 513.
[4] J. Elson, *J. Chem. Educ.*, 1969, **46**, 86.
[5] J. Elson, *J. Chem. Educ.*, 1969, **46**, 28.