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Normalized Binding Ability of Elements

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Molar atomization energy of oxides and halides (per 1 mole of cation) is found to be directly proportional to the square root of the cation valence, $E^\circ_a/m = A\sqrt{z}$. It is suggested that coefficient A be considered a *normalized binding ability of an element*, thus making possible the comparison of various elements at the same z. Periodicity of A is pointed out.

Recently (*1*) a new relation linking the length R and the atomization energy E of the individual bond in oxide crystals has been established:

$$E = J\frac{dz}{R - R_0} = \frac{E^\circ_a}{m}\frac{d}{R - R_0}, \quad (1)$$

where coefficient J is equal to the standard atomization energy E°_a of the simple oxide M_mO_n of the considered cation producing a bond with oxygen, divided by the number m of cations in the formal molecule of this oxide and by cation valence z. R_0 and d are empirical parameters related to the absolute ionic radii ρ_0 (ρ'_0 for anions) (*2*):

$$R = \rho_0 + \rho'_0 \quad (2)$$

$$d = 0.1350 - 0.0056z - 0.0347\rho_0 - 0.0050\rho_0 z. \quad (3)$$

Values of J for various cations, based on thermochemical data from literature (*3*) are listed in (*1*) and those of ρ_0 in (*2*). As Eq. (1) is also valid for crystals of highly covalent bonds and for some molecules the terms "cation" and "anion" are used conventionally, for convenience only.

The author believes that Eq. (1) could be made more compact. In search of such a form let us consider the term E°_a/m.

As shown in Fig. 1 E°_a/m appears to be a linear function of $\sqrt{z}$:

$$\frac{E^\circ_a}{m} = A\sqrt{Z}. \quad (4)$$

If we assume that Eq. (4) is valid for all the elements, A [kcal mole^{-1} vu$^{-1/2}$] could be considered as a *normalized binding ability of an element*. Indeed, using A, we are able to compare the entire binding energy of various elements with oxygen at constant z.

Due to the lack of experimental data the E°_a/m vs $\sqrt{z}$ lines may be drawn only for a limited number of elements. But believing that Eq. (4) has a general significance one can calculate

$$A = \frac{E^\circ_a}{m\sqrt{z}} = J\sqrt{z} \quad (5)$$

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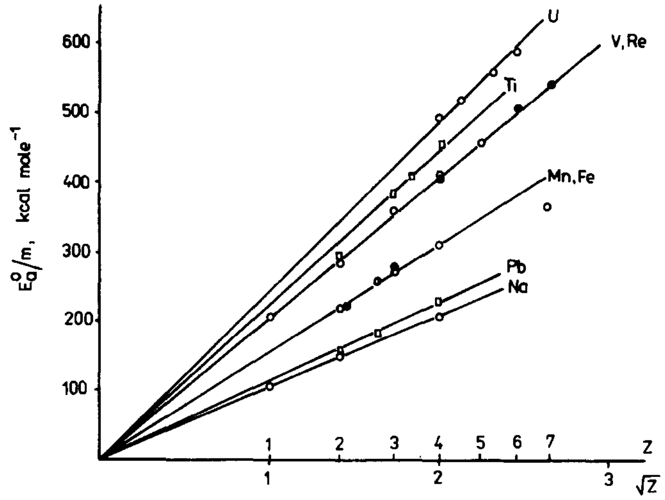

FIG. 1. Dependence of the molar atomization energy of oxides (per 1 mole of cation) on the square root of cation valence.

even in the case when E_a^o is known for only one oxide of an element. If E_a^o is accessible for two or more oxides an average A may be determined. Making use of J's listed in (2) the values of A have been calculated for a number of elements and shown in Fig. 2. From Fig. 2 we see that A reveals an interesting periodicity.

1. A increases significantly at the beginning of each period and reaches a maximum for the element of the third or fourth column, independent of the fact whether

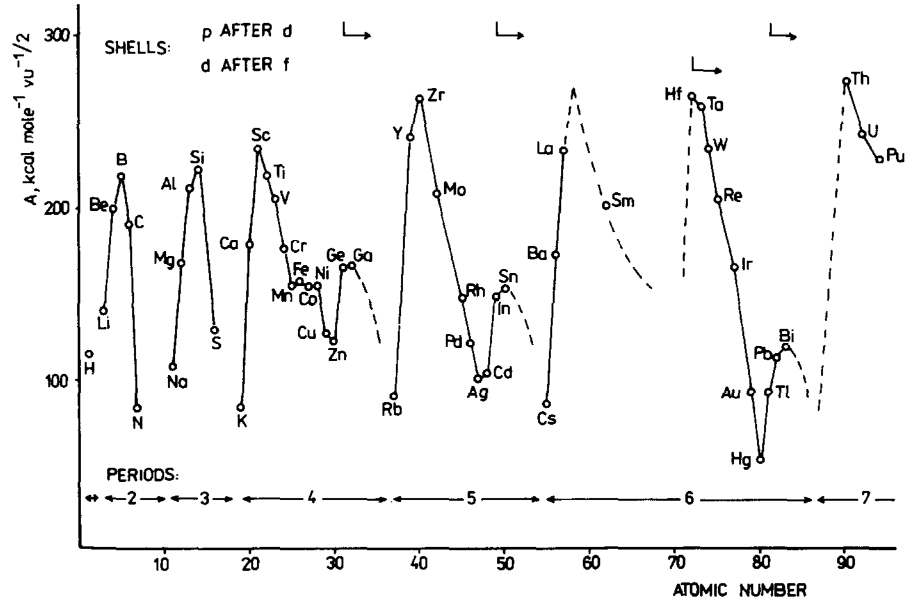

FIG. 2. Periodicity of the normalized binding ability of elements with oxygen.

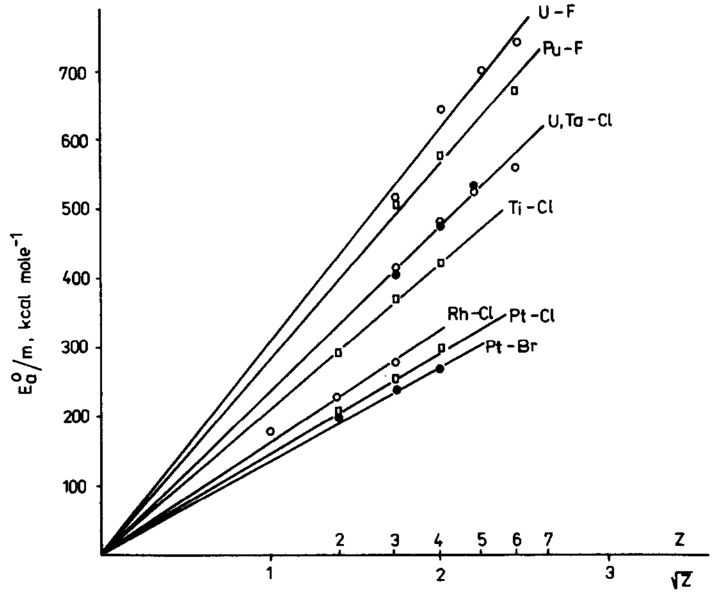

FIG. 3. Dependence of the molar atomization energy of halides on the square root of cation valence.

this element belongs to *p*, *d*, or (presumably) *f* shells.

2. *A* increases significantly for the first elements of the *p* shell occupied after filling the *d* shell and for the first element of the *d* shell occupied after filling the *f* shell.

3. *A* decreases with further increase of the number of electrons in *p*, *d*, and *f* shells.

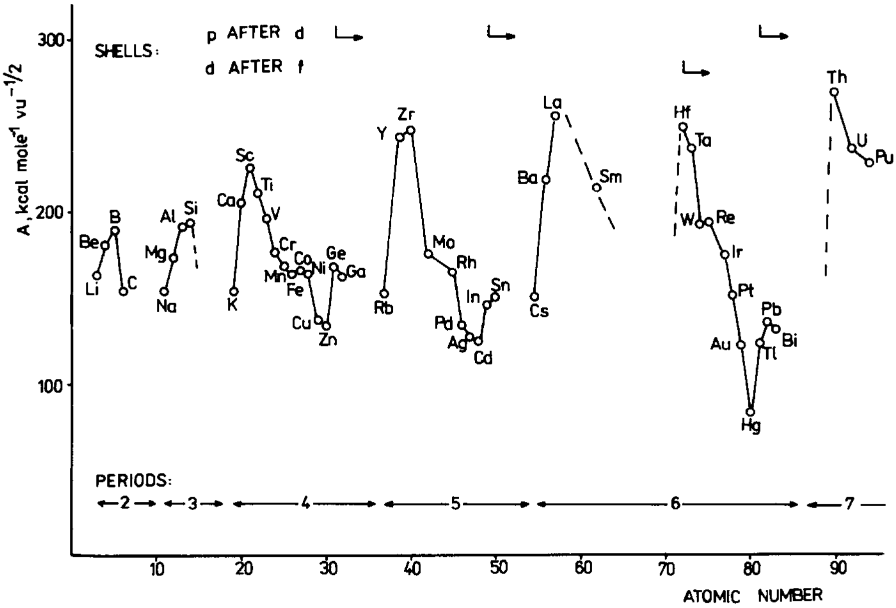

FIG. 4. Periodicity of the normalized binding ability of elements with chlorine.

4. There is therefore one maximum of A along periods 2 and 3, two maxima along periods 4 and 5, and three maxima along period 6.

In view of the above finding Eq. (1) may be written in a modified form

$$E = A\frac{d\sqrt{z}}{R - R_0}. \tag{6}$$

For comparison Fig. 3 shows the E_a°/m vs $\sqrt{z}$ dependencies for some halides, proving that they also fulfill Eq. (4). Figure 4 proves that the coefficient A for the element–chlorine bonds shows essentially the same periodicity as that found for element–oxygen bonds (Fig. 2), the differences consisting mainly in a slightly smaller amplitude of the changes for the latter.

This work, similarly to the results of Ref. (**1**), clearly demonsrates that interesting and useful relations between various properties of elements can be discovered when the state of atomization is taken as one of reference.

References

1. J. Ziółkowski and L. Dziembaj, *J. Solid State Chem.*, **57**, 291 (1985).
2. J. Ziółkowski, *J. Solid State Chem.* **57**, 269 (1985).
3. O. Kubashewski, E. L. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon, Oxford/Elmsford, N.Y. (1974).