

The Cesium Ratio, a Simple Charge Density Calculation

Chemistry is *not* an exercise in *sheer memory*. Most teachers are looking for ways to help students to reason from basic principles rather than to memorize. Beginning chemistry students rely heavily upon family resemblances and the relationships between atomic structure and chemical properties. "Abnormal" properties are particularly troublesome, especially if reasonable explanations are not forthcoming.

The anomalous properties of the 2nd period elements (Li, Be, B, etc.), including the "diagonal relationship," can be attributed to the relatively small sizes of their ions and the resulting large ionic charge density values. Crystal ionic radii have been calculated for most of the elements.^{1, 2} Unfortunately, these numbers taken by themselves are rather unimpressive. Even scale drawings showing the relative sizes of various ions fail to impress students with the magnitude of these effects. A simple calculation has been found to be helpful in dramatizing the effect of size on the intensities of the electrical fields produced by charged ions.

The "cesium ratio" is defined as *the ratio of the ionic charge of any real or theoretical ion to that of a cesium ion*. Typical calculations are illustrated in Table I. For example the volume of a magnesium(II) ion is calculated from its radius, 0.65 Å by substituting this value into the formula for the volume of a sphere, $4/3\pi r^3$. The result, 1.15 Å³, when divided into the ionic charge, +2, yields 1.74, the ionic charge density. A similar calculation for the cesium(I) ion yields the value, 0.049. Finally, the ionic charge density of Mg²⁺ is divided by the ionic charge density of Cs⁺, 1.74/0.049 = 35, and the result, rounded off to two figures, is what we will call the cesium ratio, abbreviated "CsR."

Table 1. Calculation of Cesium Ratios

Ion	Radii Å	Charge Density = $\frac{\text{Ionic Charge}}{4/3\pi r^3}$	Cesium Ratio ("CsR")
Mg ²⁺	0.65	1.74	35
Li ⁺	0.60	1.11	23
K ⁺	1.33	0.102	2.1
Cs ⁺	1.69	0.049	1.0

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¹ PAULING, L., "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 514.

² KLEINBERG, J., ARGERSINGER, W. J., JR., AND GRISWOLD, E., "Inorganic Chemistry," D. C. Heath and Co., Boston, 1960. (Values may be found in tables of properties of elements. See index.)

Table 2 lists the final results of similar calculations for the representative elements at their maximum oxidation states.

Table 2. Cesium Ratios of the Representative Elements at their Maximum Oxidation States

Ia	IIa	IIIb	IVb	Vb	VIb	VIIb
Li ⁺ 23	Be ⁺² 320	B ⁺³ 1800	C ⁺⁴ 5700	N ⁺⁵ 18,000	O ⁺⁶ 40,000	F ⁺⁷ 100,000
Na ⁺ 5.6	Mg ⁺² 35	Al ⁺³ 120	Si ⁺⁴ 280	P ⁺⁵ 610	S ⁺⁶ 1,200	Cl ⁺⁷ 1,900
K ⁺ 2.1	Ca ⁺² 10	Ga ⁺³ 68	Ge ⁺⁴ 130	As ⁺⁵ 230	Se ⁺⁶ 390	Br ⁺⁷ 570
Rb ⁺ 1.5	Sr ⁺² 6.7	In ⁺³ 27	Sn ⁺⁴ 54	Sb ⁺⁵ 100	Te ⁺⁶ 170	I ⁺⁷ 270
Cs ⁺ 1.0	Ba ⁺² 3.9	Tl ⁺³ 17	Pb ⁺⁴ 32	Bi ⁺⁵ 61	Po ...	At ...

Anomalous Properties of Lithium

After a student has calculated the charge density of lithium ion to be some *twenty times* greater than that of cesium and *four times* the corresponding value for sodium ion, he can more readily understand its greater attraction for negative ions and polar molecules such as water. This large attraction for water molecules results in a high value for the heat of hydration of lithium ion which overcompensates for the greater chemical activity of the other alkali metals. As a result, lithium appears to be "out of place" in the activity series of metals.

Some properties of lithium such as the formation of a nitride and a carbide, the solubilities of its salts, and its tendency to react with organic compounds resemble those of magnesium rather than the other alkali metals. This illustrates the diagonal relationship: the tendency for a second-shell representative element to resemble the third-shell element of the family on its right. The CsR values in Table 2 bring out this relationship clearly. The value for lithium, 23, is rather close to that of magnesium, 35, and quite different from the values of the other alkali metals.

Alkali and Alkaline-Earth Families

The cesium ratios on Table 2 suggest that the elements of Groups I-A and II-A might advantageously be classified under three headings for purposes of study: (1) the elements with values from 1 to 10; (2) lithium and magnesium; (3) beryllium. This plan has been tried with several classes in general college chemistry and found to result in a saving of time as well as improved student performance.

The cesium ratio for beryllium, 320, is an order of magnitude greater than that for magnesium, 35. Having made these calculations, the student is less

likely to expect much resemblance between Be and Mg and suspect, instead, certain similarities in the chemistry of Be and Al, 120.

Group III Elements

The cesium ratios suggest that Al should resemble Ga, 68, to some extent but not boron, 1800. In^{+3} , 27, and Tl^{+3} , 17, should be more like Mg^{+2} , 35, and Li^{+} , 23.

Indium and thallium also form monopositive cations. The CsR value for Tl^{+} , 1.2, compares closely with those for Cs^{+} , 1.0, and Rb^{+} , 1.5, suggesting some similarities.

It is interesting to compare the CsR values for the two Group III families. The values for the scandium family (not shown in Table 2) turn out to be Sc, 21; Y, 16; La, 9.3; and Ac, 10.6. This should warn the students not to expect much resemblance between the properties of these elements and those of aluminum. The chemistry of the scandium family is largely concerned with trivalent cations, while aluminum tends toward covalency and the formation of complexes.

Covalency of the Higher Oxidation States

The extreme range of properties found in the Group IV-B elements is forcefully suggested by the cesium ratios which vary from 5700 for C(IV) to 32 for Pb(IV). By having students calculate values for Sn^{+2} , 7.2, and Pb^{2+} , 4.7, the ionic characteristics of the lower oxidation states and the covalency of the higher oxidation states may be anticipated by comparison with more familiar elements having similar CsR values.

The ridiculously high values for the higher oxidation states of elements in Groups IV to VII serve to emphasize the fact that these states cannot exist as simple ions. The lowest value, 32, belongs to Pb(IV), which can still be expected to hydrate vigorously and form covalent compounds and complexes like $\text{Mg}(\text{II})$.

When transition elements are studied, interesting comparisons may be made between lower and higher oxidation states such as Mn(II) and Mn(VII). For drill, students may be given the stable oxidation states and crystal ionic radii of hypothetical elements and asked to predict chemical properties.

