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THE GLADSTONE-DALE RELATIONSHIP. PART II. TRENDS AMONG CONSTANTS

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Abstract

If the specific refractive energy constants of the Gladstone-Dale relationship are referred to the periodic table, certain trends among the constants for constituents in groups and periods become apparent. Within groups, the values of the constants generally decrease with increasing atomic number. Within periods, the relationships are more complex. These trends enable constants for other constituents to be determined by interpolation or extrapolation. Constants for Au_2O(0.152), Fr_2O(0.115), RaO(0.120), CeO_2(0.205), PoO_2(0.175), UO_2(0.100) and PoO_3 (0.150) have been determined from these trends. Alternative values for Hg_2O(0.134) and Y_2O_3(0.195) have also been estimated. A constant for S^{2-}(0.628) to be used only for silicates is proposed.

Sommaire

Les constantes de réfractivité molaire de la loi de Gladstone-Dale montrent certaines tendances générales si l'on considère les éléments d'un groupe ou d'une période du Tableau de Mendéléev. Pour les éléments d'un même groupe la constante diminue lorsque le numéro atomique augmente; pour les éléments d'une période, la relation est plus compliquée. Ces fonctions permettent, par interpolation ou extrapolation, de prédire la valeur de la constante pour les éléments intermédiaires ou voisins; c'est ainsi que nous avons pu établir les constantes des oxydes suivants: Au_2O(0.152), Fr_2O(0.115), RaO (0.120), CeO_2(0.205) PoO_2(0.175), UO_2(0.100) et PoO_3(0.150). Des valeurs nouvelles ont également été estimées pour Hg_2O(0.134) et Y_2O_3(0.195), ainsi qu'une constante pour S^{2-}(0.628) à utiliser uniquement pour les silicates qui contiennent du soufre.

(Traduit par la Rédaction)

Introduction

In his discussion of the Gladstone-Dale relationship and its constants, Larsen (1934) made some general statements about the relationships among the constants. He noted that "... for most radicals, the value of k is near 0.20." Presumably, he was referring to such constituents as CO_2, SiO_2, SeO_2, TeO_2, N_2O_5, P_2O_5, Cl_2O_5, V_2O_5, As_2O_5 Br_2O_5, Sb_2O_5, I_2O_5, SO_3, CrO_3, SeO_3, MoO_3, TeO_3 and WO_3. However, only six of Larsen's constants for these eighteen constituents are within 10% of 0.200. Using the constants for these constituents given by Mandarino (1976), only seven out of eighteen are within 10% of 0.200. Thus, Larsen's first general statement about the constants does not seem to warrant further consideration.

Larsen also noted that with regard to such groups as the univalent oxides, divalent oxides, etc., "There is a tendency for the value of k in each group to decrease as the molecular weight increases, but there are many exceptions." This statement bears closer scrutiny because if relationships among the constants can be determined, the values for other constants may be predicted.

The Constants and the Periodic Table

This second observation by Larsen is illustrated in Figure 1a where Larsen's k values for the univalent oxides are plotted against the molecular weights of the oxides. The value of k decreases from H to Li to Na. It increases from Na to K to Cu, but again decreases from Cu to Rb. From Rb to Ag it again increases and then decreases from Ag to Cs. From Cs to Hg it in-

TABLE 1. ADDITIONAL GLADSTONE-DALE CONSTANTS

Component	Atomic number	Molecular weight	k	Remarks
Au_2O	79	409.94	0.152	extrapolated
Hg_2O	80	417.18	0.134	alternative
			0.144	calculated
Fr_2O	87	462.00	0.115	extrapolated
RaO	88	242.00	0.120	extrapolated
Y_2O_3	39	225.81	0.195	alternative
			0.170	calculated
CeO_2	58	172.12	0.205	estimated
PoO_2	84	242.00	0.175	extrapolated
UO_2	92	270.03	0.100	estimated
PoO_3	84	258.00	0.150	extrapolated
S^{2-}	16	32.06	0.628	calculated†

† pertains to S-bearing silicates only

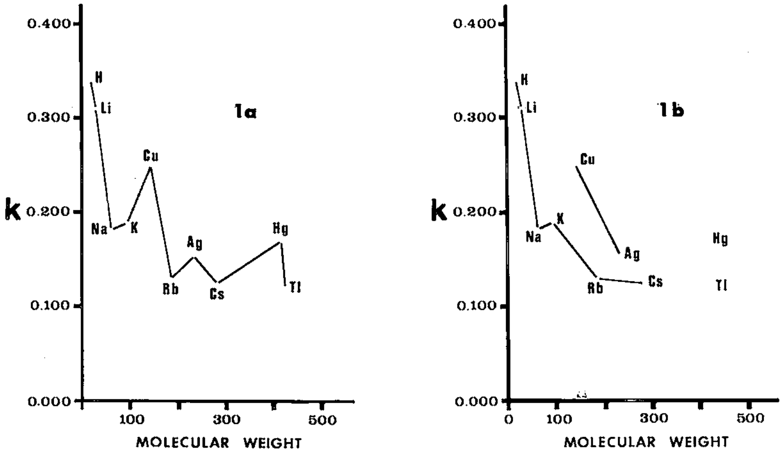

FIG. 1. Larsen's constants for the oxides of univalent elements plotted against molecular weights of the oxides; 1a (left) points connected in sequence; 1b (right) points connected according to groups in the Periodic Table.

creases and then decreases from Hg to Tl. Most of these reversals disappear if the points are connected differently as shown in Figure 1b. There, the points representing the Group IA elements (H, Li, Na, K, Rb and Cs) are connected by one line and the Group IB elements (Cu and Ag) are connected by a different line. Since Hg and Tl do not fall into either Group IA or Group IB, they are shown as isolated points. The only reversal in *k* is that which occurs between Na and K.

If the points are referred to the periodic table, certain relationships emerge. In the remaining sections of this paper, only the constants given by Mandarino (1976) are used. In the following figures, *k* has been plotted against the atomic number of the element in the constituent rather than against the molecular weight of the constituent. This eliminates the well-known reversals in molecular weights such as that between cobalt and nickel.

Several constants not included in Table 3 of Part I of this series are listed in Table 1. The table also includes alternative values for Hg_2O and Y_2O_3.

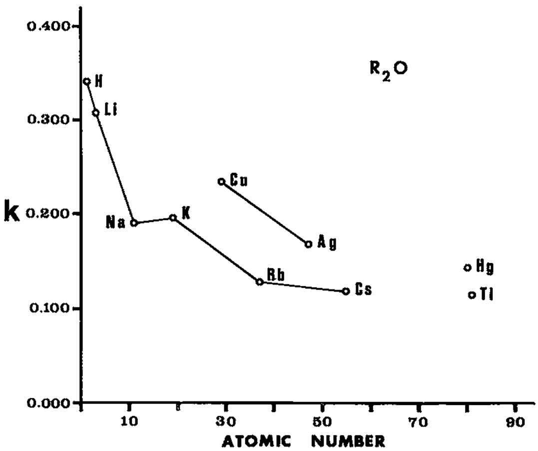

FIG. 2. The constants for the oxides of the univalent elements plotted against the atomic numbers of the elements.

The univalent elements

Figure 2 shows the relationships between the constants of the oxides of the univalent elements and the atomic numbers of the elements. The points representing the elements of Group IA (H, Li, Na, K, Rb and Cs) are connected by a line and another line connects the points which represent the elements of Group IB (Cu and Ag). The elements Hg and Tl, which belong to neither of these groups, are shown as isolated points.

For the first three constituents of Group IA (H_2O, Li_2O and Na_2O) the relationship between *k* and atomic number is essentially linear. The relationship amongst the constants for K_2O, Rb_2O and Cs_2O, although not linear, is represented by a gradual decrease in *k* with respect to atomic number. A discontinuity occurs between Na and K for which the author has no explanation. As will be seen later, the same kind of discontinuity occurs between Mg and Ca in the divalent elements. In each case the discontinuity occurs between an element in Period 3 and one in Period 4. It should be noted that univalent Tl, which acts like the elements of Group IA, fits in nicely with the general trend.

Moving to Group IB, it is apparent that the line connecting Cu to Ag is practically parallel to the line connecting K and Rb (K and Cu are in Period 4; Rb and Ag are in Period 5). If the same trends exist in Group IB as in Group IA, it should be possible to predict the value of a constant for Au_2O. In addition to being in Group IB with Cu and Ag, Au also belongs to Period 6 with Hg and Tl. There are two approaches for determining the value of k for Au_2O: one related to Group IB and the other related to Period 6. If a line is drawn from the point representing Ag parallel to the line between Rb and Cs, it will intersect the atomic number of Au (79) at a k value of 0.152. If the constant is derived from the data for Period 6 a different value is found. As will be seen later, the relationships between constants of constituents in a given period are linear with respect to atomic number. Consequently, the constants for Au_2O, Hg_2O and Tl_2O should fall on a straight line. If a line is drawn through the points Hg and Tl it will intersect atomic number 79 at a k value of 0.173. If this value is used for Au_2O the line from Ag to Au will slope upwards, a condition which does not occur in any group except VIIA (the halogen elements). Also, the k for Hg_2O was calculated from only a few compounds with rather high refractive indices, which introduces large errors in the value. Because of these reasons, the author favors the value of 0.152 for Au_2O. A linear relationship among Au, Hg and Tl can be established if the k for Hg_2O is reduced from 0.144 to 0.134. This is a reasonable reduction considering the possible error in the calculated constant.

Because the slope of the line from Rb to Cs is very gentle it follows that the line from Cs to Fr (atomic no. 87) will also have a slight slope. The probable value of k for Fr_2O is about 0.115.

The divalent elements

Figure 3 shows the constants for the divalent elements plotted against atomic number. In the Group IIA elements (Be, Mg, Ca, Sr, Ba) the relationship of the constants with respect to atomic number is very similar to that seen for the Group IA elements. The discontinuity between Mg and Ca has already been mentioned. The Group IIB elements (Zn, Cd, Hg) also show trends similar to those seen for the Group IB elements. In addition to the elements of Groups IIA and IIB, Figure 3 shows data for elements in Period 4 (V, Cr, Mn, Fe, Co, Ni, Cu) and elements in Group IV A (Sn and Pb).

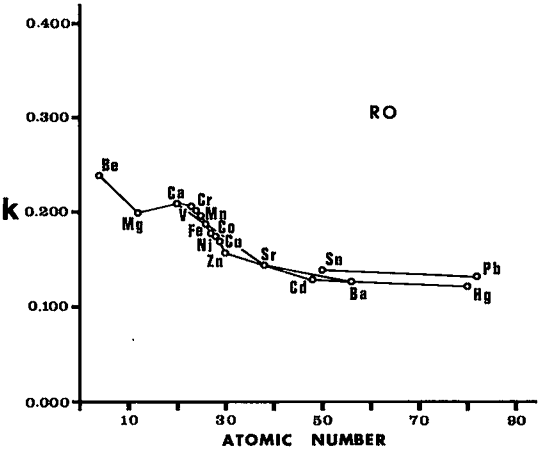

FIG. 3. The constants for the oxides of the divalent elements plotted against the atomic numbers of the elements.

In Period 4, the constants for MnO, FeO, CoO, NiO, CuO and ZnO were calculated from the data for Tutton's salts as explained in Part I of this series. The value for CaO was calculated from numerous compounds containing this constituent. With the values of these constants established, it was then possible to derive by interpolation the constants for VO and CrO. The points for the elements of Period 4 (excluding Ca) cluster about a straight line whose equation (determined by linear regression) is $k = 0.3660 - 0.0069N$, where k is the Gladstone-Dale constant and N is the atomic number.

By assuming that SnO is related to CdO in the same way that PbO is related to HgO, the constants for SnO was derived as 0.140. By extrapolating from the point for Ba to atomic number 88, the constant for RaO was found to be about 0.120.

The trivalent elements

The trivalent elements plotted in Figure 4 display a number of simple relationships. The constants of the Group IIIA elements (B, Al, Ga, In, Tl) show a practically linear relationship with respect to atomic number. Whereas elements of Group IIIB (Sc, Y, La) show the usual trend of decreasing k with respect to atomic number, it is quite possible that the value for Y_2O_3 (0.170) may be too low. A better value might be about 0.195. Until precise data for compounds containing major amounts of Y_2O_3 become available, the value of k for Y_2O_3 must

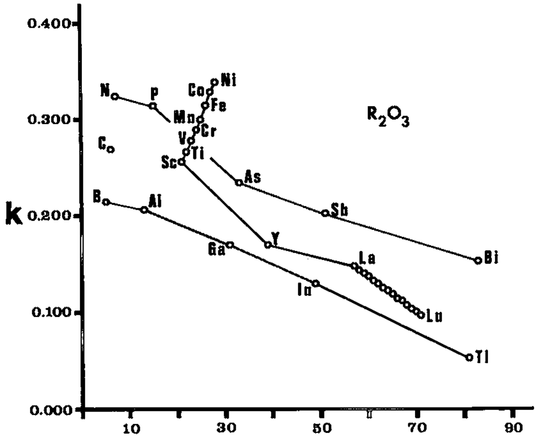

FIG. 4. The constants for the oxides of the trivalent elements plotted against the atomic numbers of the elements.

remain in question. The data for 14 of the 15 rare-earth elements plot on a practically straight line; the constant for $Pm_2O_3(N = 61)$ can be interpolated as 0.133.

Constants for the elements of Group VA (N, P, As, Sb, Bi) are also shown in Figure 4. Three of these (As, Sb and Bi) were calculated from physical data. The values for N and P were determined in the following manner. The elements B, C and N fall into Period 2 and when plotted against the atomic numbers of the elements, the constants for B_2O_3, C_2O_3 and N_2O_3 should fall on a straight line. A line was drawn through the points for B and C until it intersected atomic number 7. This point of intersection established a k value of 0.325 for N_2O_3. The point representing P_2O_3 was found by drawing a line through the point Al parallel to the line through B, C and N. This line intersected the atomic number of P(15) at a k value of 0.315. It can be seen that these values for N_2O_3 and P_2O_3 are reasonable if they are compared to the values of As_2O_3, Sb_2O_3 and Bi_2O_3. Connecting all five points with lines gives a curve very similar to that for Group IIIA.

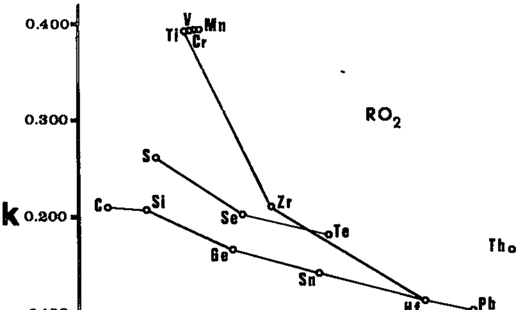

FIG. 5. The constants for the oxides of the tetravalent elements plotted against the atomic numbers of the elements.

The elements of Period 4 (Sc through Ni) fall on a straight line, as shown in Figure 4. The line was drawn through the points for the calculated constants of Sc_2O_3, Mn_2O_3 and Fe_2O_3. The constants for Ti_2O_3, V_2O_3 and Cr_2O_3 were found by interpolation; those for Co_2O_3 and Ni_2O_3 by extrapolation.

The tetravalent elements

The relationships among the tetravalent elements are quite simple, as shown in Figure 5. The Group IVA elements (C, Si, Ge, Sn, Pb) fall on an almost straight line. The elements of Group IVB (Ti, Zr and Hf) follow the usual B Group trend.

The Group VIA elements (S, Se and Te) also follow a rather simple trend almost parallel to the appropriate parts of the Group IVA curve. A value for PoO_2 can be estimated by extrapolation from TeO_2 and PbO_2 to be about 0.175.

The constants for the other members of Period 4 (Ti, V, Cr, Mn) fall on an almost horizontal line. The value for CrO_2 was found by interpolation.

The only other constant shown in Figure 5 is that for ThO_2. It is shown as an isolated point, as it falls into none of the groups or periods already discussed in this section. Related to ThO_2 are two other constituents whose constants should be of value: UO_2 and CeO_2. A constant for UO_2 was estimated by comparing the constants of PbO_2, PoO_2 and ThO_2. The ratio of the constants for UO_2 and ThO_2 is inferred to be the same as the ratio of the constants for PbO_2 and PoO_2. The constant for UO_2 derived in this way, 0.100, is considered to be a useful approximation until data become available to calculate a constant. The constant for CeO_2 should have about the same relationship to the constant for SnO_2 as the constant for ThO_2 has to that of PbO_2. The value of k for CeO_2 estimated in this way is 0.205.

The pentavalent elements

Constants for eleven oxides of pentavalent

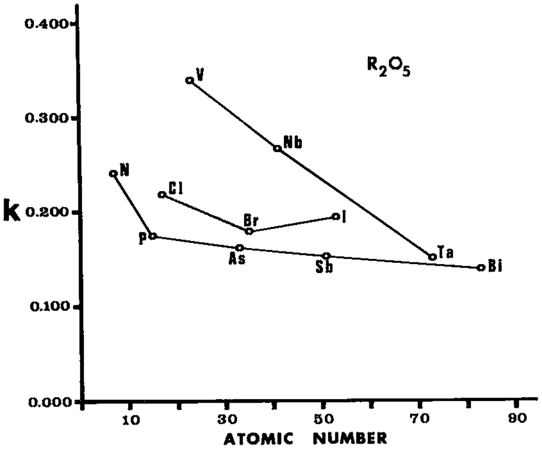

FIG. 6. The constants for the oxides of the pentavalent elements plotted against the atomic numbers of the elements.

elements are plotted against atomic number in Figure 6. Of the elements in Group VA, constants were calculated for N_2O_5, P_2O_5 and As_2O_5. The constants for Sb_2O_5 and Bi_2O_5 were found by extrapolation. This was done on the basis that all previous curves for Group A elements followed the same general trends with successively shallower slopes for the heavier elements. Thus, a line was drawn from the point labelled As until it intersected the atomic weight for Sb. This line had a slope slightly less than that of the line between P and As. A line of even shallower slope was then drawn from point Sb until it intersected the atomic number of Bi.

The points representing Group VB elements (V, Nb, Ta) fall on an almost straight line. The data for some of the elements of Group VIIA are also shown in Figure 6. Note that there is a distinct reversal in slope for the line from Br to I compared to the line from Cl to Br.

The hexavalent elements

The oxides of the hexavalent elements are those from Group VIA (S, Se, Te) and Group VIB (Cr, Mo, W) and U. As shown in Figure 7, the constants for both groups follow the usual simple trends. The curve for Group VIA can be extrapolated to a value of 0.150 for PoO_3. The point for UO_3 is shown isolated from either of these groups.

The heptavalent elements

Only five constants are plotted in Figure 8. Two of these, for Mn_2O_7 and S_2O_7, are represented as isolated points. The points for Cl_2O_7, Br_2O_7 and I_2O_7 are connected since the elements of these oxides belong to Group VIIA. Data were available for the calculation of constants for Cl_2O_7 and I_2O_7 only. The constants for Br_2O_7 was estimated by assuming that it would bear the same general relationship to Cl_2O_7 and I_2O_7 as Br_2O_5 bears to Cl_2O_5 and I_2O_5.

Elements with negative charges

The constants for the halide ions are plotted against atomic number in Figure 9. The relationships among the constants are the most complex of any group.

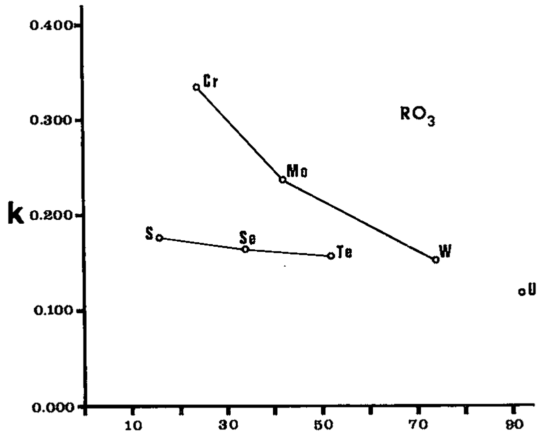

FIG. 7. The constants for the oxides of the hexavalent elements plotted against the atomic numbers of the elements.

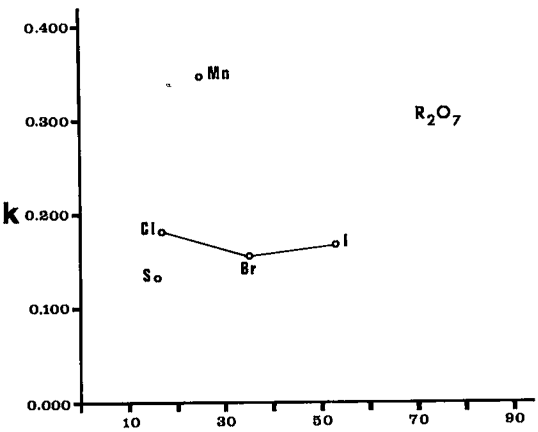

FIG. 8. The constants for the oxides of the heptavalent elements plotted against the atomic numbers of the elements.

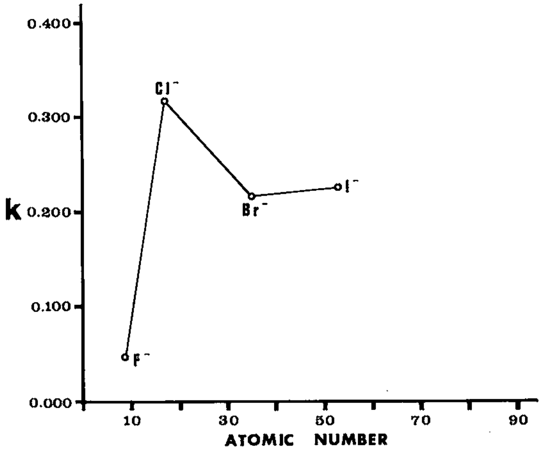

FIG. 9. The constants for the halide ions plotted against the atomic numbers of the elements.

Constants for O^{2-} and S^{2-} were also calculated. The constant for oxygen (0.203) must be used in calculations involving minerals which contain F^-, Cl^-, Br^-, I^-, or S^{2-}. Examples will be given in Part III of this series. The constant for S^{2-} is 0.628. This value was derived from the sulfur-bearing silicates helvite, genthelvite and danalite. It should only be applied to similar minerals and not to sulfides or sulfosalts.

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