

³ We have defined predissociation in possibly a slightly more specialized sense than that first used by Henri and Teves, *Nature*, **114**, 894 (1924).

⁴ See e.g., Kronig, *Zeits. Physik*, **50**, 360 (1928); Rice, *Phys. Rev.*, **33**, 748 (1929).

⁵ Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927), **50**, 617 (1928); Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928); Rice, *Comptes Rendus, Réunion Internationale de Chimie Physique*, Paris, October, 1928.

⁶ Ramsperger, *J. Am. Chem. Soc.*, in press.

⁷ Ramsperger, *Ibid.*, **50**, 123 (1928).

⁸ Bourgin, *Proc. Nat. Acad. Sci.*, **15**, 357 (1929).

⁹ Abstract No. 127 presented to the American Physical Society at the Washington meeting, April 18-20, 1929.

THE VALENCE OF SULFUR IN DITHIONATES

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It has been shown by Lindh¹ and others² that the shift in the K absorption edges for various compounds of sulfur, chlorine, phosphorous, iron, and some other substances, depends chiefly on the valence of the element in a given compound. With increasing valence in a given element the wave-length of the edge shifts to smaller values. Stelling³ has explained the effect of valence as being due to the screening effect of electrons in external parts of atoms. To be sure, other factors influence the position of the edges, such as other elements occurring in the compounds, and lattice structure, but these factors produce in general only minor fluctuations around a mean value, whereas the mean values for the several valences show rather wide divergences. For example, the wave-lengths of the principal K edge of a large number of 4- and 6-valent inorganic sulfur compounds practically all lie within half an X-unit of the means of their respective groups, whereas the means themselves are separated by 8 X. U. A similar state of affairs is observed in the 2-valent compounds. The edges do not lie quite so close to the mean, but the mean is 13 X. U. from that of the 4-valent compounds. All the substances thus far investigated bear out the general statements above.

In view of the rather large body of facts now before us, it seems legitimate to try to use x-ray absorption data to obtain information on the valence state of an element in a compound.

The substance used in the present investigation was potassium dithionate, the object being to determine the state of the two sulfur atoms in $K_2S_2O_6$. Lindh⁴ has already shown that for $Na_2S_2O_3$ and some other thio-sulfates there is not just a simple absorption edge, but two edges, corre-

sponding in position to the valence states S_{IV} and probably S_{IV} , which states are generally assumed by chemists for the two sulfur atoms in the thiosulfates. Now if valence is calculated in the usual way, then on the assumption that the sulfur atoms of the dithionates are in the same state we get for them a valence of V, and we would expect to find the K absorption edge corresponding to a single state, rather than the two edges shown by the thiosulfates.

In the present work we found as a matter of fact only one edge for $K_2S_2O_6$, and its position lies between Lindh's measurements for 4- and 6-valent sulfur. Lindh's mean values are:

S_{VI}	K_1	4987.9 X. U.
S_{IV}	K_1	4996.0 X. U.
Our present measurements show for $K_2S_2O_6$		
S	K_1	4992.8 X. U.

This result, intermediate between the usual values of S_{IV} and S_{VI} , seems to indicate that the sulfur atoms are equivalent. Our view is supported by the space group determination⁵ of the same compound, and also by the general chemical behavior of the dithionates.

The exposures were made in an x-ray vacuum spectrograph of the Siegbahn type, using a slowly rotating crystal of calcite as analyzer. The absorbing screen consisted of finely powdered potassium dithionate on tissue paper, inserted between the slit and the crystal. The slit width was slightly under 0.1 mm., and the distances of crystal from slit and plate, respectively, were each about 18 cm. The wave-length we give is based on Lindh's value for K_2SO_4 . We made comparison plates, using this material, and determined the shift by noting the distance of the edges from a mechanical reference line photographed at the same place on each plate.

The absorption edges so obtained leave something to be desired in sharpness, as they appear rather fuzzy under the comparator. The difficulty of determining the proper location of the edge has been discussed by Stelling.⁶ The ordinary comparator method was used, and later another method, which will be briefly described. The two plates to be compared for shift are mounted at right angles to each other, one of them being fixed to a carriage which can be moved by a micrometer screw. Beams of light, after passing normally through the two plates, are made parallel by means of a half-silvered surface between two prisms, and the two beams before entering the prisms are cut off by straight edges in such a way that any lines or edges to be compared are viewed directly end to end. The reference lines can be brought easily and accurately into juxtaposition, and the shift in edge can then be measured directly by turning the micrometer until the edges coincide. If the edges are of about the same degree of fuzziness (and in the present case they appeared to be so),

it is no longer necessary to speculate on their proper location. The method suffers from the difficulty usual in comparators—lack of contrast—but is rapid and direct and permitted us to duplicate readings to within 2 or 3 hundredths mm., corresponding to a wave-length difference of about two or three tenths of an X. U.

¹ Siegbahn, *Spectroscopy of X-rays*, Chap. V., 1925.

² Otto Stelling, *Zs. Phys.*, 50, 506, 1928; Aoyama, Kimura, and Nishina, *Zs. Phys.*, 44, 810, 1927; G. A. Lindsay and H. R. Voorhees, *Phil. Mag.*, 6, Suppl., 910, 1928.

³ Otto Stelling, loc. cit.

⁴ Siegbahn, loc. cit.

⁵ M. Huggins, *Phys. Rev.*, 31, 916, 1928.

⁶ Otto Stelling, loc. cit.

STUDIES ON THE GROWTH OF ROOT HAIRS IN SOLUTIONS.
THE pH MOLAR-RATE RELATION FOR BRASSICA
OLERACEA IN CALCIUM SULPHATE

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Earlier studies* upon the elongation of root hairs in solutions of single calcium compounds by C. H. Farr and W. K. Farr have shown a very delicate reaction of these particular cells to concentrations of the salt as well as to the various hydrogen-ion concentrations of the solutions used. By means of an apparatus constructed especially for the investigations, seedlings of uniform length and equal age were kept in flowing solutions of definite hydrogen and hydroxyl-ion concentrations, for periods of about twenty hours. Temperature conditions were maintained between 19°C. and 21°C. throughout the series of experiments. The work was carried on in basement dark rooms of the Marine Biological Laboratory at Woods Hole, Mass., during the summers of 1925, 1926 and 1927. By means of special micrometer eye-pieces readings were taken at ten-minute intervals for three hours daily upon the rate of elongation of aquatic root hairs. Careful observations upon other features of root development were also made and were compared with the root-hair development.

The complete absence of growth of root hairs in pure distilled water, along with the definite rates of growth in different concentrations of Ca(OH)₂, established at the outset a basis for the comparison of the behavior of root hairs in the presence and in the absence of the cation, Ca. Subsequent experiments in solutions of CaCl₂ and Ca(NO₃)₂ furnished data concerning the rates of growth in the presence of an additional anion.

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