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EFFECT OF CHEMICAL COMBINATION ON THE ABSORPTION OF X-RAYS AT WAVE-LENGTHS ON EACH SIDE OF THE K DISCONTINUITY

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Abstract

The difference in the absorption of x-rays by iodine in the free state as compared to that of iodine in the chemically combined state, was investigated for wave-length bands on each side of the K absorption limit of this element. The method used was the double ionization chamber method, with the x-ray bands obtained by voltage control and filters. The results indicate that on the long wave-length side of the K limit, the absorption coefficient of the chemically free iodine atom is about 0.3 percent greater than that of the combined atom, while on the short wave-length side of the K limit, the reverse is indicated with a difference of about 0.5 percent. Silver was also investigated, but from the few measurements obtained, the absorption coefficient of the chemically free silver atom as reduced from AgCl by sunlight, seems to be greater than that of the combined silver atom in the AgCl before reduction, for wave-length bands on each side of the K limit of silver.

I. Introduction

IN VIEW of recent work done by W. B. Morehouse[1] which showed an apparent effect of chemical combinations on the absorption of x-rays, it was thought of interest to continue work on this problem to ascertain what effect x-rays of wave-lengths in the region of the K absorption limit might show. Accordingly one of the chemical reactions used by Morehouse was selected and data were obtained for bands of wave-lengths on each side of the K limit of iodine. This reaction may be represented as follows:

$$I_2+Na_2S_2O_3\rightarrow 2NaI+Na_2S_4O_6$$

in which the I_2 was in alcohol solution and the $Na_2S_2O_3$ in an aqueous solution, as described later.

The method used was essentially the same as that used by Morehouse; i.e., the absorption of two solutions placed in an x-ray beam was measured, after which the solutions were allowed to react chemically and the absorption after reaction was measured. The densities before and after reaction were also measured and taken into consideration in calculating the effect. The separation of the x-rays into groups on each side of the K discontinuity was accomplished by voltage control and filters. A preliminary attempt was made to use crystals to obtain homogeneous beams but this was abandoned after it was shown that the effect sought was less than the experimental error involved in this method.

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[1] W. V. Morehouse, Phys. Rev. **29**, 765 (1927).

In addition to the iodine reaction, another reaction was used, in which the reduction of AgCl was accomplished by light without disturbing the absorbing materials in the path of the x-ray beam.

II. Experimental Procedure

Figure 1 shows a plan of the general features of the apparatus used. There was little difference between the general method employed in making observations and that used by Becker,[2] Read,[3] and Morehouse.[1] The two ionizations chambers *C* and *C′* received x-ray beams 1 and 2 which passed through slits *S* and *S′* respectively. There was impressed across the two chambers a potential of 540 volts with its mid-point grounded so that when the separate ionization currents were equal they neutralized each other and there was no deflection of the electrometer needle. This was connected, as shown, to the collecting rods of the ionization chambers. The chambers were filled with methyl bromide to increase their absorption of the x-rays in the usual manner. Amber was used for insulating the collecting rods and quartz for insulating the wire connecting the rods to the quadrant electrometer *Q*. The electrometer was of the Compton type and was used at a sensitivity of 5000 to 7000 mm/volt.

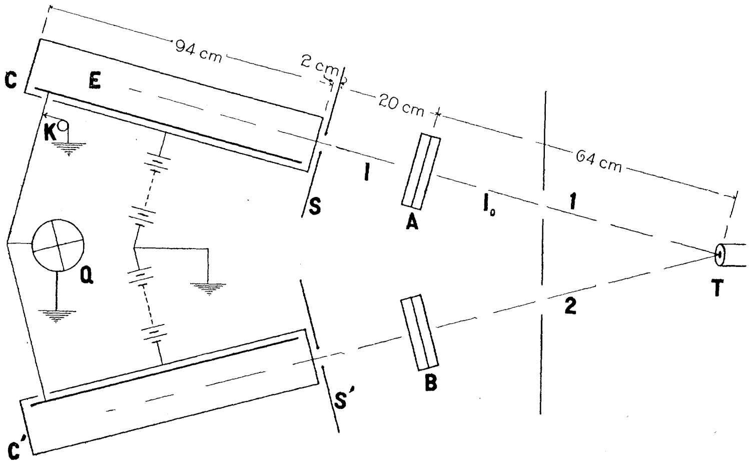

Fig. 1. General plan of apparatus.

The slit *S* was adjusted for a reading by noting when the electrometer needle showed the same drift with x-rays entering the chambers as when they were not. This zero drift could not entirely be eliminated but it was thought that by the above method true settings were obtained despite this drift.

In the path 1 of the x-ray beam was placed a two-compartment cell *A*, the walls of which were made of 0.16 cm bakelite and washed with melted

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[2] J. Becker, Phys. Rev. **20**, 134 (1922).

[3] H. Read, Phys. Rev. **27**, 373 (1926).

paraffin. Each compartment was 1 cm thick. A similar cell B was placed in path 2. The cells were placed far enough from the slits to make the amount of scattered radiation that passed through the slits from the cells, small compared to the transmitted beam itself.

The beams on entering the ionization chambers were limited only by the slits S and S' and the size of the focal spot on the target, so that the energy passing through the slit was proportional to the area of the slit, or for a constant length slit, to the slit width. This was measured by means of a micrometer screw and could be read to 0.0001 inch. The maximum size of the slit bounded a beam which, at the rear of the ionization chamber, subtended an area of about 2×3 cm, the edges of which were well away from the side walls of the chamber.

A lead screen confined the x-rays to the general direction of the two beams. The tube was placed so that the target was symmetrically situated with respect to each beam; i.e., the tube was placed so that each beam made the same angle with the face of the target.

The general procedure in making observations was as follows:—the tube was put in operation and then the density of each separate solution was measured by means of a Westphal balance, while the tube was reaching steady operation. The first balance was obtained with nothing in either path and this was repeated at the end of the run as a check measurement on the apparatus. Then cell B containing the solutions was placed in beam 2, empty cell A was introduced into beam 1, and S was adjusted to make a balance, i. e. to re-establish the initial electrometer drift. This reading of slit S is called S_0 in what follows. Cell A was then filled with the two separate solutions, the iodine solution being placed in the compartment nearest the slit in all cases as it was thought this would help to make the results more comparable. Also, cell A was always used in beam 1. With the filled cell in beam 1, a balance was made and repeated several times. This slit width is called S_1. Then cell A was removed from the path of the x-rays and the cell's contents were poured into a beaker to react, after which the mixed solution was put into the cell and the cell replaced in the x-ray beam. A balance was again made and repeated several times and this slit width is called S_2. Now as a third condition, cell B was removed and its solutions allowed to react and then replaced, when another balance was obtained. This latter condition may be considered the equivalent of that represented by S_1 and as such was used in calculating the results. Finally the densities of the mixed solutions in each cell were measured.

The iodine reaction:

$$I_2+N_2S_2O_3\rightarrow 2NaI+Na_2S_4O_6$$

changed the iodine from the free state in which it was in a 70 percent alcohol solution (12.7 gm I to 1000 cc of 70 percent alcohol) to the combined state with sodium (NaI) still in solution; the reaction of the I-alcohol solution with an equal amount of sodium thiosulfate solution (25 gm $[Na_2S_2O_3+5H_2O]$ to 1000 cc H_2O) being complete. 160 cc of each solution were used in each cell.

In addition to the iodine reaction with the solutions in bakelite cells, silver chloride was used in the form of an emulsion on paper as supplied by the Eastman Kodak Company under the trade name of "Solio" paper. This paper was cut into sheets 5×7 cm in size and these placed back to back in pairs in slots cut in the walls of a light tight box so that between pairs was a space of about 1 cm. Each box contained twenty sheets of "Solio". When the lid of the box was opened, light could be directed at an angle upon the sensitive surfaces of the "Solio" thus causing a darkening of the emulsion, or a reduction of the silver chloride, until the paper became quite dark, or as it customarily appears when used for making photographic "proofs". Exposure to x-rays apparently does not effect the emulsion within a time period of several hours. The face of the box was covered by a thin glass plate sealed on with paraffin, and the open ends of the box were sealed over with two layers of black paper, while all cracks and openings were well coated over with shellac, so that after the "Solio" sheets had been placed in the box they were hermetically sealed within it. This was done to prevent any liberation of chlorine that was not held in the gelatine of the emulsion, from the path of the x-rays, and also to prevent any change due to humidity variation. Two such boxes were used, one in each beam, and slit widths S_1 (papers in each box, unexposed), S_2 (papers in box in beam 1, exposed), and S'_1 (papers in each box, exposed) were observed. To produce blackening, sunlight was used and directed to the surface of the "Solio" by means of a heliostat and suitably placed mirrors so that the boxes were not disturbed in the x-ray beams during the entire run.

Filtered beams of x-rays were obtained uuder the following conditions:

Case (a): Cu filter 0.050 cm thick; tube voltage 60 k.v.$_{\text{eff}}$; mean wave-length = 0.24A.

Case (b): Cu filter 0.033 cm thick; tube voltage 49 k.v.$_{\text{eff}}$; mean wave-length = 0.30A.

Case (c): Al filter 0.74 cm thick; tube voltage 44 k.v.$_{\text{eff}}$; mean wave-length = 0.34A.

Case (d): No filter; tube voltage 22 k.v.$_{\text{eff}}$; Mo target; K lines of Mo most prominent; mean wave-length = 0.70A.

The effective mean wave-length of each of the filtered bands of x-rays was approximately determined by finding the effective mass absorption coefficient of a particular thickness of Al for the several bands, and then referring to Richtmyer's tables[4] to find the wave-length that corresponded to the coefficient so obtained. This wave-length was considered the effective wave-length of the filtered band.

As a check on this determination, curves were plotted for each band by extrapolating the curves of Behnken[5] and applying the absorption data of Richtmyer's tables for each filter. These distribution curves showed peaks somewhat less in wave-length than the wave-lengths obtained as the effec-

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[4] F. K. Richtmyer, Phys. Rev. **18**, 13 (1921).

[5] Behnken, Zeits. f. Physik **3**, 48 (1920).

tive mean wave-lengths by the first method. However, this shift is to be expected since the longer wave-lengths are relatively more absorbed in the ionization chamber, and, since the effect of the Al plate is to harden the rays that enter one chamber, a too large value of the absorption coefficient is obtained; and thus the mean effective wave-length will be somewhat larger for the absorption method than for the graphical method. However, the agreement is fairly close and is as shown in Table I.

TABLE I. *Comparison of Al plate method with the graphical method.*

Case	Mean effective wave-length of x-ray band By Al plate method	 By graphical method
a	0.24A	0.23A
b	0.30	0.275
c	0.34	0.30

The plotted distribution curves were compared, with apparent consistancy, to those given by Mertz[6] in his use of filtered bands of x-rays. These curves showed a width of about 60 percent of the peak wave-length when measured between the wave-lengths of half the energy value of the peak wave-length.

In case (a) values were obtained by using for the first pair of trials a water-cooled Mo target tube, but for the other trials a W target tube was used. This latter tube was also used for cases (b) and (c).

APPENDIX TO PROCEDURE

An attempt was made to carry out the foregoing general procedure by using beams of homogeneous x-rays as obtained by use of rock-salt crystals, one being placed in each beam about midway between the cell and the tube target.

Crystals 7 cm long were used and no limitation was put on the beam other than that determined by the size of the crystal face. At the small angles of incidence desired this produced a reflected beam less than 1 mm wide and as homogeneous as necessary for this work; i.e. the difference in wave-length between the rays reflected by the extreme outside edges of the crystal was about 0.06A. After the set-up had been calibrated for wave-length, angle of crystal setting and ionization chamber position, it was found that the highest accuracy obtainable was about 0.3 percent in slit width settings. This may have been due to the small energy present in the beam, although a particular setting seemed definite enough in itself and not difficult to make, but once made would not remain a balanced setting for more than a few seconds. A shift of the focal spot would cause a relative difference in the energy of the two beams by producing a relative change in the wave-lengths of the two beams since the beams hit the crystals at slightly different relative angles than before the focal spot shifted. This difficulty might be somewhat overcome by having both ionization chambers in practically the same direction as by having them side by side or one above the other, and by using two adjacent crystals mounted for this arrangement.

Also, if the x-ray energy available were sufficient to permit a fixed slit or pin hole to be placed in front of the target, the angle of incidence of the beam on the crystal face would be fixed, thus eliminating variation of the direction of the reflected beam or relative change in energy in the beams because of changed wave-length. This latter variation might be minimized by using a tube voltage so that the maximum of the energy distribution curve occurs at the desired wave-length. For this present work so high a tube voltage was not available.

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[6] P. Mertz, Phys. Rev. **28**, 891 (1926).

III. Discussion of Formulae

Referring to the Fig. 1 let I_0 represent intensity of the x-ray beam 1 before reaching cell A, and let I be the intensity of the beam after passing through the cell A and incident on slit S. Also let E be the ionization current in chamber C. E is proportional to S, the slit width, and to I, the intensity of the incident beam; i.e., in arbitrary units, $E=SI$.

Now $I=I_0e^{-\alpha x}$ where e is the base of the natural logarithms; α is the absorption coefficient, defined in the usual way; and x is the thickness of the absorbing layer. If we let $\alpha x=\mu$, which may be called the absorption *constant* (to distinguish it from α, the absorption coefficient) we have

$$I=I_0e^{-\mu}. \tag{1}$$

In this case μ includes the absorption *constants* of all the absorbing media making up the cell and its contents, or $\mu=\mu_1+\mu_2\cdots$. To put μ in terms of the atomic absorption coefficient, let $\mu=\tau nx$, where τ is the apparent absorption coefficient per atom; n is the number of atoms per cc; and x is the thickness of the absorbing layer as above defined. Then letting $nx=N$, the total number of atoms in the path of the beam of unit cross section area, we have: $\mu=\tau N$; and from (1):—

$$I=I_0e^{-\tau N}. \tag{2}$$

In the particular measurements made first with the empty cell A in beam 1 and with cell B plus solutions in beam 2,

$$E=S_0I=S_0I_0e^{-\tau_cN_c} \tag{3}$$

where (τ_cN_c) is the absorption constant for the cell walls alone, and S_0 is the observed slit width.

Then with the separate solutions in cell A in beam 1, and cell B plus solutions as before in beam 2,

$$E=S_1I_0e^{-\tau_cN_c-\tau_1N_1} \tag{4}$$

where τ_1 is the apparent average atomic absorption coefficient; N_1 is the number of these so-called average atoms of solution in the path of the beam per sq. cm; and S_1 is the observed slit width. This summing of the absorption constants of the different absorbers in the beam was proved to be justifiable in Morehouse's paper[1] above referred to.

Since the ionization current in chamber C' is the same for the condition represented by equation (3) and for that represented by equation (4) (except for variation in the tube itself which should effect each beam in the same proportion), we can combine (3) and (4).

$$S_0I_0e^{-\tau_cN_c}=S_1I_0e^{-\tau_cN_c-\tau_1N_1}$$

or

$$S_0=S_1e^{-\tau_1N_1}. \tag{5}$$

Similarly in the case of the mixed solutions:

$$S_0 = S_2 e^{-\tau_2 N_2} \tag{6}$$

where τ_2 is the apparent average atomic absorption coefficient for the mixed solution; N_2 is the number of these average atoms in the path of the beam, per sq. cm; and S_2 is the observed slit width.

Expressing equation (5) in logarithmic form

$$\log (S_0/S_1) = -\tau_1 N_1$$

or

$$\tau_1 = -(1/N_1) \log (S_0/S_1)$$

and

$$\tau_2 = -(1/N_2) \log (S_0/S_2).$$

Let

$$\tau_1 - \tau_2 = \Delta\tau = -(1/N_1) \log (S_0/S_1) + (1/N_2) \log (S_0/S_2)$$

and

$$\frac{\Delta\tau}{\tau} = \frac{(1/N_2) \log (S_0/S_2) - (1/N_1) \log (S_0/S_1)}{(1/N_1) \log (S_0/S_1)}$$

or

$$\frac{\Delta\tau}{\tau} = \frac{N_1(\log S_0 - \log S_2)}{N_2(\log S_0 - \log S_1)} - 1.$$

If we assume that N is proportional, in each case, to the average density, then $N_1/N_2 = \rho_1/\rho_2$ where ρ represents the density of the solutions. This assumption seems valid since no new kinds of atoms are introduced into the path of the beam between measuring the absorption of the separate solutions and that of the mixed solution. Therefore the equation

$$\frac{\Delta\tau}{\tau} = \frac{\rho_1}{\rho_2} \frac{(\log S_0 - \log S_2)}{(\log S_0 - \log S_1)} - 1 \tag{7}$$

gives the fractional change in the atomic absorption coefficient due to the chemical reaction. This formula was used in computing from the data, the effect shown in the results.

IV. Results for Iodine

The results obtained from the observed data are given in the Table II. In this table the first column of figures refers to the trial number of each run; the second column gives the values in percent of the relative change in the average atomic absorption coefficient of iodine for a filtered band of x-rays of mean wave-length equal to 0.24A, as previously described in section II for case (a); the remaining columns present the values obtained for other cases in the same way, using different filtered bands of x-rays of mean wave-lengths as indicated and as also previously described under section II.

The positive values of the percent change in the atomic absorption coefficient mean that τ for the combined iodine atom is greater than τ for the free iodine atom.

TABLE II.

Trial	Case *a* $\lambda_m=0.24$A	Case *b* $\lambda_m=0.30$A	Case *c* $\lambda_m=0.34$A	Case *d* $\lambda_m=0.70$A
1	+0.47%	+0.09%	+0.15%	−0.34%
2	+0.52	+0.29	+0.72	−0.28
3	+0.45	+0.27	+0.25	−0.33
4	+1.09	+0.91	+0.74	−0.30
5	+0.48	+0.27		
6	+0.77	+0.39		
Av.	+0.63	+0.37	+0.47	−0.31 (−0.36)*
Av. deviation of the mean	±0.08	±0.08	±0.13	±0.01

* This value was obtained by Morehouse for about the same band of x-rays, viz. with a Mo target at 21 k.v. $_{eff}$, and no filter.

V. RESULTS FOR SILVER

The results of measurements on the change in absorption of Ag, by reducing the Ag from AgCl photochemically, are rather uncertain and hardly more than an indication that there is a change. In this case the slit width is the only measurement that need be considered, since density changes do not enter, as these can occur only in the direction of the beam and so do not change the total number of atoms traversed by the x-rays. In terms of slit width, the results are:

	Case a	*Case d*
$\Delta S/S=\Delta\tau/\tau=$	-0.16 percent	-0.23 percent

$$\therefore\ \tau(\text{free Ag}) > \tau(\text{combined Ag})$$

VI. SOURCES OF ERROR

The results are affected by errors due to the change in total absorption being measured instead of that due to the iodine or silver alone. In the case of the iodine reaction, Morehouse[1] has shown that the absorption of iodine is about nine times that by sulphur, the only other element that changes its valence is this reaction; and therefore the observed effect may be considered mainly due to the iodine. However, Stobbe and Schmitt,[7] and more recently Batley,[8] have shown spectroscopically that iodine in alcohol solution tends to form hydrogen triiodide or other periodides, which may involve from several percent to one hundred percent of the iodine in the solution, depending upon the time and other factors. But if this occurs there would still be an effective change in valence of a large proportion of the iodine upon the formation of NaI in the reaction here used. The variation shown in the results may be due in part to this uncertainty as to the true state of the iodine in the alcohol solution. In the case of the silver reaction, all other elements in the path of the x-rays are of low atomic number and hence their change in absorption must be a small fraction of the whole change, since comparable amounts of Ag and those light elements take part in the change.

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[7] Stobbe and Schmitt, Z. wiss. Phot. **20**, 57 (1920).

[8] A. Batley, Faraday Soc. Trans. **24**, 438 (1928).

The scattering should be nearly the same before reaction as after, except for the small difference made by the change in density; but since the scattering is only a fraction of the whole apparent absorption, any changes in this should be a correspondingly small fraction of the total change observed.

Unsteadiness of the tube operation and ionization chambers was the main cause of erratic readings and the comparatively low accuracy of the results. The tube was operated on an a.c. transformer and was self rectifying. The source of a.c. was a motor generator run by a d.c. generator which in turn was operated by an a.c. motor run by the power from the university generating plant. However, the a.c. voltage applied to the tube transformer had to be constantly regulated by a manually controlled series resistance to keep its variations within 0.5 percent.

In part of the work a water cooled Mo target tube was used and with this it was noted that the rate of flow of water made a slight difference in tube current. Change in tube current and consequent change in x-ray energy in the emitted beam should have affected each beam equally and therefore should have made no difference in the slit setting for a balance. This, however, was not strictly true due probably to slight dissymmetry between the two ionization chambers. Also apparently one ionization chamber continually became relatively less absorbing with respect to the other chamber, thus causing the balancing slit width to gradually become narrower with time, due possibly to unequal activity of the methyl bromide in the two chambers. Differential temperature changes between the two chambers were minimized by connecting the chambers with a rubber tube, and by covering each chamber with about 7 cm thickness of cotton waste.

Errors in the slit width readings were less than 0.004 percent and back lash in the micrometer screw was accounted for by always approaching a balance setting from the same direction.

Measurement of density was made by the Westphal balance and was in itself to an accuracy of 0.01 percent but after the solutions reacted, due to the heat of reaction the temperature of the mixture rose several degrees and slowly returned to that of the room. Too long a wait between the slit readings for the separate solutions and the mixed solution could not be permitted because of tube and ionization chamber variation, and so readings were made on the warmer mixed solution, and an effort made to measure its density at the temperature at which it had been used. Evaporation of the lighter solvent (alcohol) during the slit measurement would also introduce error into the density measurement made somewhat later. This total density measurement error might be as large as 0.05 percent.

Error might also be incurred by relative changes in the cell widths. This was the first serious error encountered and it was found that a variation of 15 percent in slit width was produced in five hours time by simply filling one cell with the solution and letting it stand in position in the x-ray beam for that length of time. Apparently the iodine or the alcohol or the combination attacks the bakelite and causes warping. Other materials were then sought but nothing with sufficiently low absorption in the desired region of x-ray wave-lengths and that would withstand the iodine solution, could be found, so melted paraffin was poured into the bakelite cells and then immediately poured out, leaving a thin coating on the inside surface of the cell. This appeared to prevent any effects of the solution on the cell walls.

These errors together made the results certain to no greater accuracy than 0.08 percent.

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