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A Spectrophotometric Investigation of the Interaction between Antimony(III) and (V)[1a,b,c] in Hydrochloric Acid Solutions

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Introduction.—The investigations described here are concerned with the nature of the abnormally deep and intense coloration that exists in some systems containing an element in two different oxidation states or in a "mixed" oxidation state. Hofman and Resencheck[3] first emphasized the general occurrence of this phenomenon in connection with studies of the ferri ferrocyanides. Earlier, Werner[4] had expressed his feeling that there was an analogy between the intense color of quinhydrone and the intense colors of various mixed compounds of platinum (II) and (IV), with cyanide, chloride, bromide, oxalate and ammonia as coördinating groups. Many authors have commented on the significance of this phenomenon for the theory of the color of inorganic compounds.[5,6,7,8,9,10]

The color of an ion is of course in general a function of its environment. However, the coloration referred to above that exists in some systems that can be said to contain an element in two different oxidation states is so much more intense than the color of either component in most other systems that it deserves recognition as a special phenomenon. We shall use the term "interaction absorption" for this effect. For purposes of illustration, we mention a few of the systems which exhibit this effect. In solution in hydrochloric acid, mixtures of the ions of copper(I) and (II),[11] of antimony(III) and (V),[12] of tin(II) and (IV),[13] and of iron(II) and (III),[11] are all much more intensely colored than are the components at the same concentration. In the solid state, the ferri ferrocyanides appear to be much more strongly colored than the brown ferri ferricyanides or the colorless ferro ferrocyanides. A mixed precipitate of iron(II) and iron(III) hydroxides is almost black, compared to the red-brown color of ferric hydroxide; similarly a mixed precipitate of cerium(III) and cerium(IV) hydroxides is blue, compared to the slight yellow color of hydrated ceric oxide. The bluish-black Cs_2SbCl_6[14] and black Rb_2SbCl_6[12] (formally compounds of antimony(IV)) are to be compared with the light yellow-green $RbSbCl_6$[15] and the colorless complex chlorides of antimony(III) with the alkali metal chlorides.[16] The black substance, cesium aurous auric chloride,[17,18] is similarly more colored than most of the complex chlorides of aurous or auric gold. The isomorphous salt $Cs_2AgAuCl_6$ which is believed to contain argentous silver and auric chloride is also jet black. This fact is included to emphasize that there are conditions other than the presence of an element in several oxidation states which can produce unusually intense coloration.

It is possible to continuously vary the composition of a solution, but seldom possible to do this for a solid. Furthermore it is much easier to carry out accurate spectrophotometric measurements for solutions than for solids. We have therefore chosen to study the effect of some of the concentration variables on the interaction absorption of hydrochloric acid solutions of antimony(III) and antimony(V). Exploratory measurements of the absorption spectra of mixed tin(II) and (IV) solutions, and of arsenic(III) and (V) solutions, were also made.

Experimental.—Absorption spectra of solutions were measured using a Beckman Model DU quartz spectrophotometer. The absorption cells were the usual rectangular right prism type of quartz cells with a 10-mm. light path. Quartz spacers were available to reduce the light path to one millimeter. In order to protect the spectrophotometer from acid vapors, the loosely fitting Beckman cell covers could be sealed to the cells with a molten one to one mixture of beeswax and rosin.[19]

The optical density, D, reported here is equal to $\log_{10} I_0/I$. Extinction coefficients are defined by $\epsilon = D/cl$, where l is the light path in centimeters and c is the concentration of the absorbing solution in volume molal units.

The antimony solutions were prepared by dissolving approximately known quantities of reagent grade antimony trichloride or pentachloride in measured quantities of concentrated hydrochloric acid of known titer to give solutions of known final volume.[20]

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(1) (a) For a preliminary report of this work see THIS JOURNAL, **69**, 2076 (1947); (b) presented in part at the 115th meeting of the American Chemical Society, San Francisco, Calif., April, 1949; (c) a more detailed account of these investigations is contained in the thesis by James E. Whitney, submitted in partial fulfillment of the requirements for the degree of Master of Science at the California Institute of Technology, June, 1948.

(2) Present address: Kellex Corporation, New York 7, N. Y.

(3) Hofman and Resencheck, *Ann.*, **342**, 372 (1905).

(4) Werner, *Z. anorg. Chem.*, **12**, 53 (1896).

(5) Hoffman and Höschsele, *Ber.*, **48**, 20 (1915).

(6) Wells, *Am. J. Sci.*, **3**, 417 (1922).

(7) Biltz, *Z. anorg. allgem. Chem.*, **127**, 169 (1923).

(8) Stieglitz, *Proc. Nat. Acad. Sci.*, **9**, 309 (1923).

(9) Zintl and Rauch, *Ber.*, **57**, 1739 (1924).

(10) Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(11) We are unable to quote references for the original discoveries of interaction absorption in these cases. Further work on these systems has been carried out in these Laboratories. Doehlmann and Fromherz (*Z. physik. Chem.*, **A171**, 377 (1934)) have published absorption spectra of mixed Cu^I and Cu^{II} halide solutions.

(12) Weinland and Schmid, *Ber.*, **38**, 1080 (1905).

(13) Present research.

(14) Setterberg, *Oefversigt. Kgl. Vetenskapsakad. Förhandl.*, **6**, 22 (1882).

(15) Weinland and Feigl, *Ber.*, **36**, 244 (1903).

(16) Gmelin–Kraut, *Handbuch der anorg. Chem.*, 7th Edition, Vol. III, part 2, p. 743.

(17) Wells, *Am. J. Sci.*, **3**, 315 (1922).

(18) Elliott and Pauling, THIS JOURNAL, **60**, 1846 (1938).

(19) Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938, p. 554.

(20) The concentrations quoted herein are in volume formal (*F*) or volume molal (*M*) units.

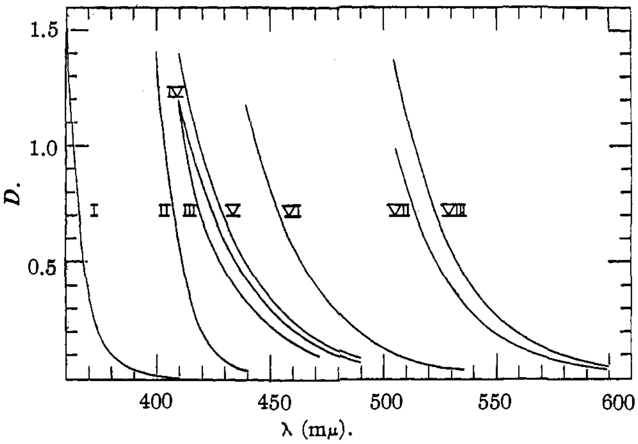

Fig. 1.—Absorption spectra of:

	I	II	III	IV	V	VI	VII	VIII
Sb(III)	0.30	0	0.068	0.22	0.16	0.03	1.17	0.745
Sb(V)	0	0.28	0.23	0.087	0.14	1.41	0.30	0.725

I–V, 11.3 F HCl; VI–VIII, 10.3 F HCl.

Aliquots (*ca.* 0.002 F in antimony) of the stock solutions were analyzed for antimony by a coulometric titration of antimony(III) (by means of electrolytically generated bromine).[21] Antimony(V) was determined after reduction with sulfur dioxide. Excess sulfur dioxide was removed from the solution by boiling.

For the preliminary measurements reported here, solutions of Sn(II) and Sn(IV) were obtained by dissolving reagent grade $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$ in concentrated hydrochloric acid. Arsenic solutions were made by dissolving "primary standard" arsenious oxide, As_2O_3, in concentrated hydrochloric acid. The formal concentration of the hydrochloric acid, calculated on the assumption that the arsenious oxide was converted to the trichloride, was adjusted by the addition of weighed amounts of dry hydrogen chloride. The arsenic(V) solution was obtained from the arsenic(III) solution by oxidation with chlorine.

Spectrophotometric Results for Antimony Solutions in Concentrated Hydrochloric Acid.—Figure 1 illustrates the general nature of interaction absorption for antimony solutions in concentrated hydrochloric acid. Curves I and II are for *ca.* 0.3 F solutions of antimony(III) and antimony(V), respectively; curves III–V are for mixtures of these two solutions. Pure antimony(III) absorbs in the near ultraviolet and appears colorless to the eye. Antimony(V) solutions absorb on the fringe of the visible region and are a pale yellow in color. The 1:1 mixture of 0.3 F solutions (Curve V) is a medium yellow, and more strongly absorbing than the other mixtures for this constant total concentration. Curves VI–VIII are for antimony solutions at a total formality of 1.5. The color of the 1:1 mixture is a deep orange-brown. Comparison of Curves V and VIII reveals that for 1:1 mixtures a fivefold increase in the concentration of antimony causes a much greater increase in D at any wave length.

We define D_i, the optical density of interaction absorption, by the equation

$$D_i(\lambda, C_{III}, C_V) = D(\lambda, C_{III}, C_V) - D(\lambda, C_{III}) - D(\lambda, C_V) \quad (1)$$

In this relation, $D(\lambda, C_{III}, C_V)$ is the observed optical density (corrected to 1.00-cm. path length) of the solution containing the two oxidation states at concentrations C_{III} and C_V; $D(\lambda, C_{III})$ and $D(\lambda, C_V)$ are the absorptions due to the pure components at the same concentrations, C_{III} and C_V, in a solution of hydrochloric acid of the same concentration as the mixture.

We have found that D_i, the optical density of interaction absorption, in solutions of antimony(III) and (V) in concentrated hydrochloric acid is proportional to the product of the concentrations of the antimony(III) and (V)

$$D_i = k_i(\lambda) C_{III} C_V \quad (2)$$

In Fig. 2 it is shown that when D_i for a fixed wave length is plotted as a function of $C_{III}C_V$, a straight line going through the origin is obtained. From a survey of all the data obtained, it appeared that the values of $k_i(\lambda)$ obtained in this way are constant to better than 10% for variations of the $C_{III}C_V$ product of by a factor of 10 or more. The averaged values of $k_i(\lambda)$ obtained from all the data are plotted in Fig. 3; in obtaining these data, the $C_{III}C_V$ factor has been varied from 0.5 to 0.01. The interpretation of the result expressed by eq. (2) will be discussed in a subsequent section.

One qualitative observation that is of importance for this subsequent discussion is that when a strongly colored mixed solution of antimony(III) and (V) in concentrated hydrochloric acid is cooled to −80° it remains liquid and there is no change perceptible to the eye in the color of the system.

The extinction coefficients of antimony(V) by itself in concentrated hydrochloric acid are independent of concentration—that is, in contrast to the marked optical interaction between antimony(III) and (V) molecules, there is no interaction between antimony(V) molecules. Figure 4 is a logarithmic plot of the extinction coefficients of antimony(V) in concentrated hydrochloric acid The data in the wave-length range 380–440 mμ were obtained with 0.1 and 1.0 F Sb(V) solutions using 1 and 10-mm. path lengths and the observed extinction coefficients were constant to ±3%. The optical densities of 0.3 and 0.5 F antimony(III) solutions were also observed, and these indicate that this species also obeys Beer's law. The extinction coefficients for antimony(III) are also plotted in Fig. 4.

As reported subsequently, antimony(V) solutions in 3.5 F hydrochloric acid are colorless; we have examined the hypothesis that the yellow color of antimony(V) in concentrated hydrochloric acid is really interaction absorption due to the formation of some antimony(III) by the reaction

$$Sb(V) + 2Cl^- \longrightarrow Sb(III) + Cl_2 \quad (3)$$

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[21] Brown and Swift, This Journal, **71**, 2717, 2719 (1949); *cf.* Myers and Swift, *ibid.*, **70**, 1047 (1948).

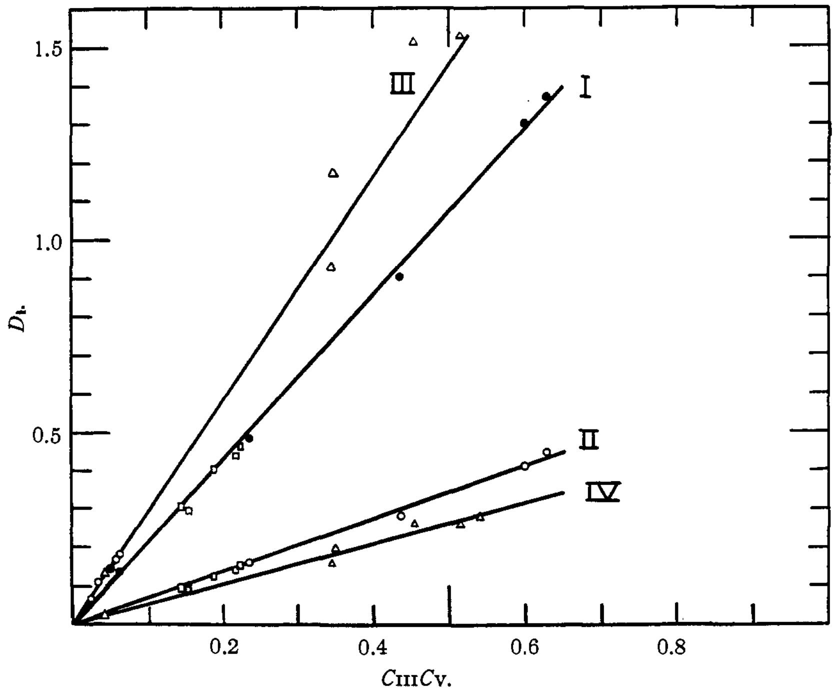

Fig. 2.—Interaction absorption, D_i, as a function of the $C_{III}C_V$ product: I, λ = 440 mμ, abscissa, 10 $C_{III}C_V$; □, total Sb = 0.3 *F*, 11.3 *F* HCl; ●, total Sb = 0.5 *F*, 10.0 *F* HCl. II, λ = 475 mμ, abscissa, 10 $C_{III}C_V$; □, total Sb = 0.3 *F*, 11.3 *F* HCl; ○, total Sb = 0.5 *F*, 10.0 *F* HCl. III, λ = 500 mμ, abscissa, $C_{III}C_V$; ○, total Sb = 0.5 *F*, 10.0 *F* HCl; △, total Sb = 1.5 *F*, 10.3 *F* HCl. IV, λ = 550 mμ, abscissa, $C_{III}C_V$; △, total Sb = 1.5 *F*, 10.3 *F* HCl.

If this were the case, the effect of the addition of chlorine would be to reverse (3), decreasing the concentration of antimony(III) and decreasing the color. Figure 5 shows that the spectrum of a 0.3 *F* antimony(V) solution saturated with chlorine is the sum of the absorption spectra of the chlorine and the antimony(V). We conclude that reaction (3) is not the cause of the color of antimony(V) in concentrated hydrochloric acid; this color is characteristic of an antimony(V)-containing ion.

Spectrophotometric Results for Antimony Solutions in 3.5 *F* Hydrochloric Acid.—As shown in Fig. 4, the extinction coefficients of antimony(III) in 3.5 *F* hydrochloric acid are independent of the antimony concentration and the same as those observed for antimony(III) in concentrated hydrochloric acid.

The extinction coefficients of antimony(V) in 3.5 *F* hydrochloric acid are dependent on a large number of variables—the time after preparation or dilution of the solution, the concentration of the antimony(V), and the presence of other ions in the solution.

We will first present the results for antimony(V) solutions that have stood long enough so that their properties are no longer a function of time. In Fig. 6, the apparent extinction coefficients of a series of such solutions are plotted as a function of the antimony concentration. For antimony concentrations greater than 0.3 *F*, the data fit an equation of the type

$$\epsilon(\lambda) = a(\lambda)c^n \qquad (4)$$

where *n* has values slightly greater than 2 for the wave lengths 330, 340 and 350 mμ.

As illustrated in Fig. 6 and Table I, the extinction coefficients of antimony(V) at a concentration of 0.1–0.2 *F* are not independent of concentration but they do not change so violently with concentration as is the case at the higher concentrations.

In the same table there are presented a series of data which illustrate the effect of added ammonium perchlorate, perchloric acid and ammonium chloride. It is seen that ammonium chloride has a more marked effect on the extinction coefficients of the antimony(V) than do ammonium perchlorate or perchloric acid.

The variable extinction coefficients of antimony(V) in 3.5 *F* hydrochloric acid as a function of antimony concentration or of chloride concentration show that more than one kind of antimony(V) complex ion with water, hydroxide and chloride exists in appreciable concentration in this medium. The equilibria among the different kinds of antimony ions are established slowly.

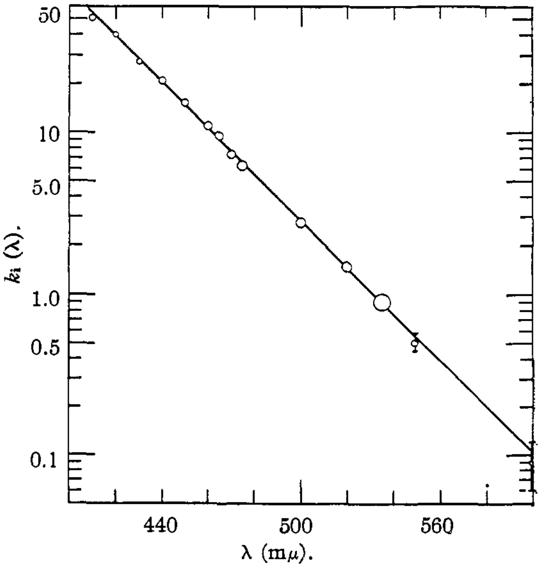

Fig. 3.—$k_i(\lambda)$ (eq. 2) as a function of wave length.

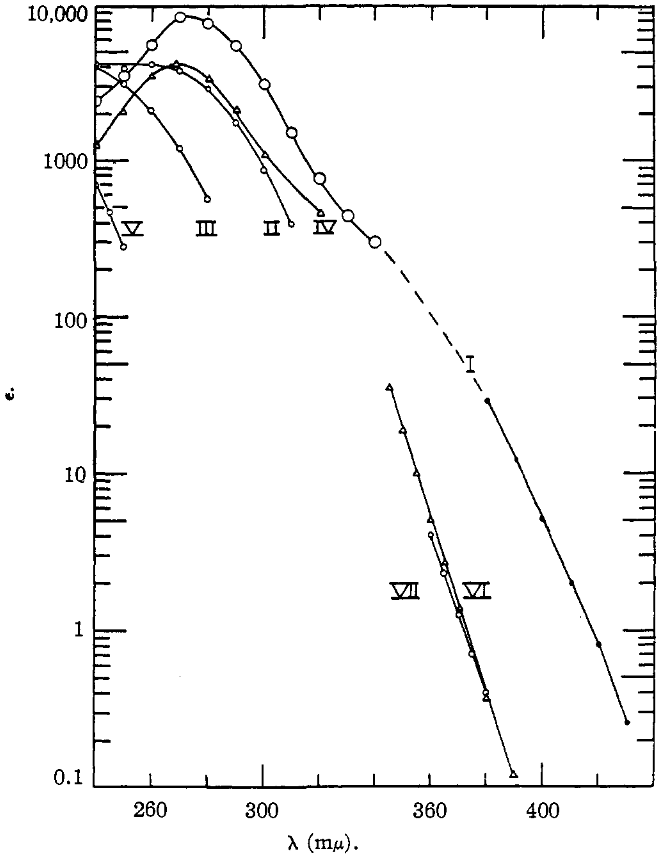

Fig. 4.—The extinction coefficients of Sb(III) and Sb(V) in various concentrations of HCl. I, Sb(V) in concentrated HCl.[a] II, 1.47 × 10^{-4} *F* Sb(V) in 6 *F* HCl immediately on dilution from 1.5 *F* Sb(V) in concentrated HCl. III, solution of curve II, 4 days after dilution. IV, 1.47 × 10^{-4} *F* Sb(V) in 3.5 *F* HCl, 3 hours after dilution from 1.5 *F* Sb(V) in concentrated HCl. V, solution of curve IV, 4 days after dilution. VI, Sb(III) in 11 *F* HCl.[b] VII, Sb(III) in 3.5 *F* HCl.[c]

[a] ○, 1.47 × 10^{-4} *F* Sb(V) in 11.6 *F* HCl; ●, the data were obtained for 0.10 to 1.0 *F* Sb(V) solutions in 10.5 *F* HCl, and agreed to ±3%.

[b] Data for 0.30 and 0.50 *F* Sb(III) solutions agreed to 4%.

[c] Data for 0.30 and 0.90 *F* Sb(III) solutions agreed to 10%.

When a concentrated antimony(V) solution (*ca.* 1.5 *F*) in concentrated hydrochloric acid is diluted to become a 0.5 *F* antimony solution in 3.5 *F* hydrochloric acid, the pale yellow color that is characteristic of the antimony(V) in concentrated acid slowly fades and it requires over five hours for the color to disappear completely. In Fig. 4 Curves II–V show a similar phenomenon for the dilution of antimony(V) solutions in concentrated hydrochloric acid to give *ca.* 10^{-4} *F* Sb(V) solutions in 6 and 3.5 *F* HCl. When a concentrated (1.0 *F*) antimony(V) solution in 3.5 hydrochloric acid is diluted with 3.5 *F* hydrochloric acid to an antimony formality of 0.3, the extinction coefficients observed shortly after dilution are intermediate between those of 1.0 *F* and 0.3 *F* antimony (Fig. 6). After a time of sixteen hours equilibrium apparently has been reached. We have not attempted to follow the behavior with time of these systems more closely.

Mixed solutions of antimony(V) and antimony(III) in 3.5 *F* hydrochloric acid that have stood for a while do not show the pronounced interaction absorption that occurs in concentrated acid. Table II lists some optical densities for a mixture containing 0.4 *F* antimony(V) and (III). These values are somewhat (but not spectacularly) greater than the sums of the optical densities of separate 0.4 *F* antimony(V) and (III) solutions. However, the extinction coefficients of antimony(V) are a function of the antimony(V) concentration, due perhaps to polymerization, to ionic strength effects, or to chloride supplied by hydrolysis of antimony pentachloride. In Table II, the special interaction between antimony(V) and (III) in 3.5 hydrochloric acid has been evaluated by assuming that the extinction coefficients of 0.4 *F* antimony(V) in the presence of 0.4 *F* antimony(III) are the same as the extinction coefficients of a 0.8 *F* antimony(V) solution. The resulting D_i's are quite small. We may therefore conclude that there may be weak "interaction absorption" of mixtures of antimony(V) and (III) in 3.5 *F* hydrochloric acid, but that this is of the same order of magnitude as the effect of other perturbations, such as ionic strength, added chloride, or other antimony(V)-containing molecules, on the absorption spectrum of antimony(V).

TABLE I

THE EXTINCTION COEFFICIENTS OF 0.1–0.2 *F* Sb(V) IN 3.5 *F* HCl IN THE PRESENCE OF VARIOUS OTHER IONS

λ, mμ	0.2 *F* Sb(V)	0.1 *F* Sb(V) 0.65 *F* NH_4Cl	0.1 *F* Sb(V) 0.5 *F* $HClO_4$	0.1 *F* Sb(V) 0.5 *F* NH_4ClO_4	0.1 *F* Sb(V)
280		109	95	88	77
290	54	53	46	43	36
300	23.6	24.2	19.8	20.2	15.9
310		10.8	8.0	9.8	4.45
320	3.45				2.3
330	1.36				1.12

TABLE II

THE ABSORPTION SPECTRUM OF A MIXED Sb(III) AND Sb(V) SOLUTION IN 3.5 *F* HCl

λ, mμ	*D*(III + V) 0.4 *F* Sb(III) 0.4 *F* Sb(V)	*D*(III) 0.4 *F* Sb(III)	*D*(V)[a]	D_i[b]
370	1.02	0.49	0.57	−0.05
375	0.66	.28	.37	+ .01
380	.45	.16	.24	+ .05
390	.228	.072	.099	+ .057
400	.133	.040	.045	+ .048

[a] *D*(V) are the calculated optical densities for 0.4 *F* Sb(V) using the extinction coefficients observed for 0.8 *F* Sb(V). [b] $D_i = D(\text{III} + \text{V}) - D(\text{III}) - D(\text{V})$.

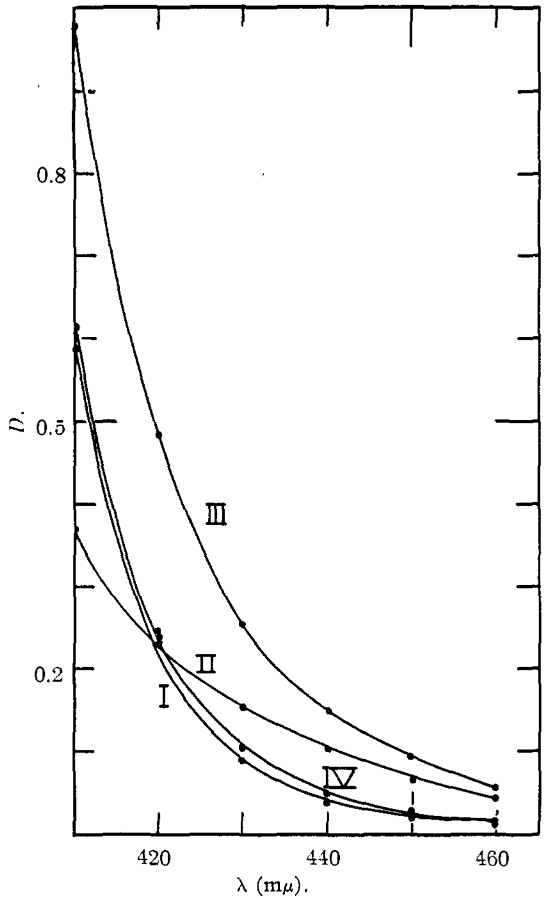

Fig. 5.—The effect of chlorine on the absorption spectrum of Sb(V) in concentrated HCl. I, 0.28 *F* Sb(V) in 11 *F* HCl; II, 11 *F* HCl saturated with Cl_2; III, 0.28 *F* Sb(V) in 11 *F* HCl, saturated with Cl_2; IV, III–II.

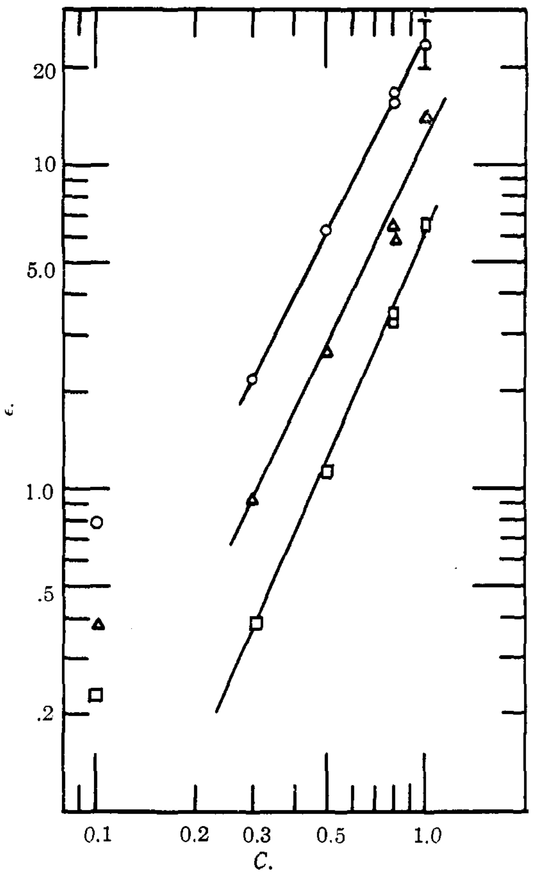

Fig. 6.—The extinction coefficients of Sb(V) in 3.5 *F* HCl as a function of antimony concentration: ○, λ = 330; △, λ = 340; □, λ = 350. The slopes of the three straight lines are: 2.06 (λ = 330), 2.16 (λ = 340), 2.28 (λ = 350).

When a 1:1 mixture of antimony(III) and (V) in concentrated hydrochloric acid at a total antimony concentration of *ca.* 1.5 *F* is diluted to become *ca.* 0.5 *F* in antimony and 3.5 *F* in hydrochloric acid, the interaction absorption color (which is much more intense than that of antimony(V) itself) does not fade immediately but loses its color in a period of about an hour. This indicates that the kind or kinds of antimony(V) molecules which exist in concentrated hydrochloric acid and which interact with the antimony(III) molecules to give rise to interaction absorption are slowly converted into "non-interacting" kinds of antimony(V) molecules in 3.5 *F* hydrochloric acid. The rate of disappearance of the intense "interaction absorption" color was greater than the rate of disappearance of the pale yellow color of antimony(V) in concentrated acid upon dilution.

Brown and Swift,[21] in these Laboratories have reported that when an antimony(III) solution in 3.5 *F* hydrochloric acid is partially oxidized with chlorine, the yellow "interaction absorption" color results but fades upon standing. This indicates that the kind of antimony(V) molecule first formed by reaction of chlorine with antimony(III) is like the antimony(V) present in concentrated hydrochloric acid in that it can give rise to "interaction absorption" and in that it is slowly hydrolyzed to a non-interacting form.

When a solution of antimony(V) in 3.5 *F* acid is warmed, a pale yellow color develops, and slowly disappears again when the solution has cooled. The more intense interaction absorption may also be reversibly generated by heating a mixed solution of antimony(III) and (V) in dilute acid.

Spectrophotometry of Tin and Arsenic Solutions.—We have investigated the absorption spectra of mixed tin(II) and (IV) and mixed arsenic(III) and (IV) solutions in concentrated hydrochloric acid. Figure 7 shows that there is marked interaction absorption for the tin mixture,[22] but that there is no marked interaction absorption for the mixed arsenic solution.

The interaction absorption for the mixed tin solution occurs in the near ultraviolet and is barely perceptible to the eye. This is presumably

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[22] A more detailed study of this case has been made by Mr. C. I. Browne of these Laboratories, and will be reported shortly.

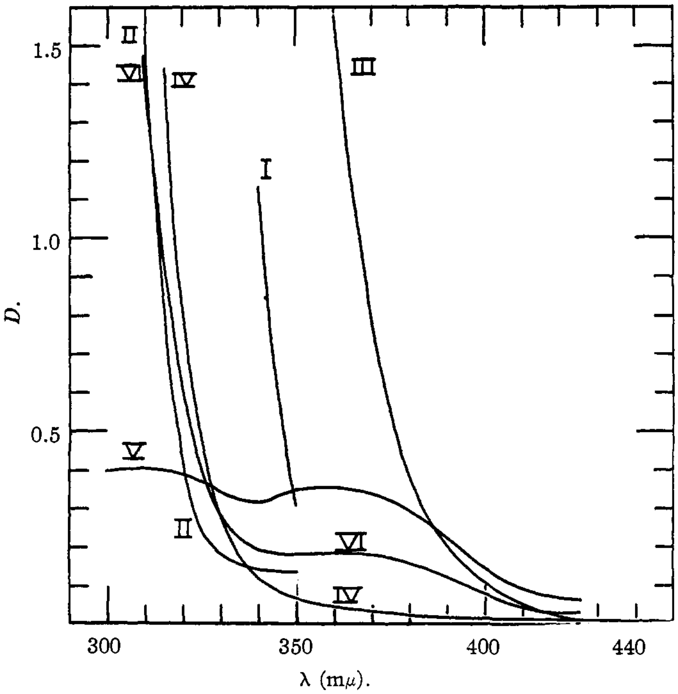

Fig. 7.—The absorption spectra of mixed As(III) and As(V), and of mixed Sn(II) and Sn(IV) solutions in concentrated HCl: I, 0.84 *F* Sn (II); II, 0.84 *F* Sn(IV); III, 0.42 *F* Sn(II), 0.42 *F* Sn(IV); I, II, III in 11.6 *F* HCl. IV, 0.76 *F* As(III); V, 0.76 *F* As(V)[a]; VI, 0.38 *F* As(III), 0.38 *F* As(V); IV, V, VI in 11.3 *F* HCl.

[a] Additional data not plotted for the As(V) solution are:

λ (mμ)	250	260	270	275
D	1.56	1.01	0.700	0.596

the reason why it has not been previously reported.

Discussion and Interpretation.—The fact expressed by equation (2) that in concentrated hydrochloric acid the optical density of interaction absorption is proportional to the product of the concentrations of the antimony(III) and (V) implies that the absorbing species is a dimeric complex containing one antimony(III) and one antimony(V). That is, the equilibrium involved in the formation of the absorbing species is of the type

$$\mathrm{Sb(III)Cl_4^- + Sb(V)Cl_6^- \rightleftarrows Sb_2Cl_{10}^-} \quad (5)$$

$$\mathrm{C(Sb_2Cl_{10}^-) = KC_{III}C_V} \quad (6)$$

rather than the type

$$\mathrm{2Cl^- + Sb(III)Cl_4^- + Sb(V)Cl_6^- \rightleftarrows 2Sb(IV)Cl_6^=} \quad (7)$$

$$C(\mathrm{Sb(IV)Cl_6^-}) = \sqrt{K'C_{\mathrm{III}}C_{\mathrm{V}}} \quad (8)$$

The equilibrium equations (6) and (8) should of course be written with activities instead of concentrations. That equation (2) fits the data so well indicates that in concentrated hydrochloric acid the appropriate activity coefficient product involving the activity coefficients of antimony(III) and (V) and of the dimer are to a good approximation independent of the total antimony concentration even when this is as high as 1.5 *F*.

The similarity of the absorption spectra of antimony(III) in 3.5 *F* and 11 *F* hydrochloric acid indicates that this component exists mainly in the same form at both acidities; this is usually assumed to be the $\mathrm{SbCl_4^-}$ ion.

We assume that the pale yellow form of antimony(V) in concentrated hydrochloric acid is the $\mathrm{SbCl_6^-}$ ion. The spectrophotometric data indicate that in 3.5 *F* hydrochloric acid, the $\mathrm{SbCl_6^-}$ ion undergoes a slow hydrolysis to a less colored ion

$$\mathrm{SbCl_6^- + {\it x}H_2O = SbCl_{6-{\it x}}(OH)_{\it x}^- + {\it x}H^+ + {\it x}Cl^-} \quad (9)$$

The qualitative observation of the effect of temperature on the color of antimony(V) in 3.5 *F* hydrochloric acid suggests that reaction (9) is exothermic. As noted below, the hydrolyzed ion, $\mathrm{SbCl_{6-{\it x}}(OH)_{\it x}}$, may be in part polymerized. It may of course also be neutralized by attachment of $\mathrm{H^+}$.

The qualitative observation that on dilution from concentrated acid, interaction absorption in a mixture of antimony(III) and (V) fades more rapidly than does the pale yellow color of the $\mathrm{SbCl_6^-}$ ion suggests that reaction (9) proceeds in several steps and that in the first of these the antimony(V) is converted to a form which is itself still colored but which is incapable of interacting with the antimony(III) to give interaction absorption; in a later step, the non-interacting but colored form of antimony(V) is further hydrolyzed to a colorless form. Because the relative rates of fading of "interaction" color and "antimony(V)" color have only been casually observed and not carefully studied, this interpretation must be regarded as a suggestion rather than a conclusion.

Brown and Swift[21] have also suggested equilibria of the type embodied in equations (5) and (9) in order to interpret their results on the electrochemical properties of the antimony(III)-(V) couple.

The variation of the optical density of antimony(V) solutions in 3.5 *F* hydrochloric acid with antimony concentration described by eq. (4) could be explained by a polymerization of the type

$$\mathrm{3Sb(OH)_6Cl_{6-{\it x}}^- \rightleftarrows (Sb(OH)_6Cl_{6-{\it x}})_3^{-3}} \quad (10)$$

It is unlikely that this simple explanation is valid in view of the marked effect of other variables, chloride concentration, acidity, and ionic strength on the spectrum of antimony(V) in 3.5 *F* acid. It may even be that the variation with antimony concentration of the extinction coefficients of antimony(V) in 3.5 *F* hydrochloric acid is due simply to a shift in the equilibrium of eq. (9) due to changes in the free chloride concentration, the acidity, and the ionic strength associated with changes in the antimony concentration.

The explanation of interaction absorption in terms of eq. (5) is in accordance with the properties of the intensely black solids, Rb_2SbCl_6, Cs_2SbCl_6, and $(NH_4)_2SbBr_6$.[23,24,25] These substances are formally compounds of antimony(IV). X-Ray analysis shows that they have the K_2SnCl_6 structure, and therefore contain crystallographically equivalent $SbX_6^=$ octahedra, in which each antimony atom is separated from neighboring antimony atoms by two non-bonded halogen atoms. However, these substances are diamagnetic; they do not contain independent Sb(IV)$Cl_6^=$ groups each having an odd electron and being paramagnetic. In the crystal, a $SbCl_6$ octahedron can interact with 12 equivalent neighboring octahedra. In solution, two antimonys must interact in a similar way; by analogy with the solids, we need not suppose that there is any halogen bridging involved in the dimerization in solution.

The fact that the data are satisfied by eq. (2) and do not require an equation of the type $C_D = K(C_{III} - C_D)(C_V - C_D)$ (where C_D is the concentration of interaction dimer) indicates that even in 1:1 mixed solutions that are 1.5 *F* in total antimony, the dimeric complex does not contain over 10–20% of the antimony. The comparatively weak color of the mixed solutions as compared to the intense black of the crystals suggests that the concentration of the dimeric "interaction" complex in solution is quite low.

It is probable that resonance between structures of the type (Sb(V)X_6^-, Sb(III)$X_6^=$) and (Sb(III)$X_6^=$, Sb(V)X_6^-) is of importance for the structure of solid M_2SbX_6 compounds and for the structure of the dimer in solution. Jensen has discussed in more detail the kinds of structure which will allow electrons to be passed back and forth between antimony atoms.[25] It is evident from the results in 3.5 *F* acid, that substitution of halogen coördination by oxygen coördination (of water or hydroxide) decreases the tendency for colored complexes of this type to form. This may be the reason why no interaction absorption was observed for the arsenic case—since it is generally believed that arsenic acid, H_3AsO_4, like phosphoric acid, is not converted to a chloroarsenic acid in concentrated hydrochloric acid. It is reasonable to assume that the positive effect observed for the tin solutions is due to interaction between chloro complexes of tin(II) and (IV).

The observation that cooling to −80° had no perceptible effect on the interaction absorption of a solution of antimony(III) and (V) in concentrated hydrochloric acid implies that there is very little heat for reaction (5). Since the entropy change in a dimerization reaction is usually negative, one would therefore expect the dimeric interaction complex not to be very stable. The M_2SbX_6 compounds are not very stable either and often decompose on attempted recrystallization. It may be that the interaction dimer is not at all a stable complex in solution but that it is "collision complex" which is formed for a very short period of time whenever an Sb(V)Cl_6^- ion and an Sb(III)Cl_4^- (or Sb(III)$Cl_6^{\equiv}$??) ion come close to each other in solution.

The following calculation is intended to indicate the plausibility of this suggestion. In the crystal of Rb_2SbCl_6, the Sb–Sb distance for neighboring $SbCl_6$ octahedra is 7.25 Å.[25] This corresponds to the closest possible distance of approach of 2 $SbCl_6$ octahedra, because in the crystal the Cl–Cl distance for chlorine atoms of neighboring octahedra is 3.6 Å., which is twice the ionic or Van der Waals radius of chlorine. If now we consider that for a given Sb(V)Cl_6^- in solution, any Sb(III)Cl_4^- (or Sb(III)$Cl_6^{\equiv}$) ion that approaches within 7.25 to 7.35 Å. will have formed a "collision complex" with the Sb(V)Cl_6^- ion, the volume of solution that could be occupied by the antimony(III) molecule while interacting with the antimony(V) molecule is $4\pi \times 7.30^2 \times 0.10 = 67$ Å.^{3} The total available volume per molecule in a 1 mole/liter solution is 1660 cu. Å. (neglecting the molal volume of the solute for this rough calculation). Therefore if there were no attractive or repulsive forces between the Sb(III) and Sb(V) molecules (other than a repulsive force on contact) the fraction of $67/1660 = 0.04$ of the Sb(V) molecules in a 1 *F* Sb(III) solution would have Sb(III) molecules within 0.1 Å. of the distance of approach of SbX_6 octahedra in the crystal. A concentration of this order of magnitude for a strongly colored dimer could account for the observed color of the mixed solutions.

If there is no marked energy of interaction in the ground state between Sb(V)X_6^- and Sb(III)$X_6^=$ in the crystal or in the solution, then the marked effect on the absorption spectrum of the system can be explained as being due to a strong interaction in the optically excited states of the system. A further discussion of this idea will be contained in subsequent contributions on this general subject.

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Summary

The absorption spectra of mixed antimony(III)

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[23] Elliott, *J. Chem. Phys.*, **2**, 298 (1934).

[24] Asmussen, *Z. Elektrochem.*, **45**, 698 (1939).

[25] Jensen, *Z. anorg. allgem. Chem.*, **232**, 193 (1937); **252**, 317 (1944).

and antimony(V) solutions, of mixed tin(II) and tin(IV) solutions, and of mixed arsenic(III) and arsenic(V) solutions, all in hydrochloric acid, have been studied. The first two systems in solution in concentrated hydrochloric acid exhibit the phenomenon of "interaction absorption."

The optical density of interaction absorption for the mixed antimony solutions is proportional to the product of the concentrations of the antimony(III) and antimony(V) implying that the absorbing species is a dimeric complex containing one Sb(III) and one Sb(V). In 3.5 *F* hydrochloric acid, there is no marked interaction absorption.

The spectroscopic results indicate that Sb(III) exists as the same ion or molecule in concentrated and 3.5 *F* hydrochloric acid but that Sb(V) undergoes hydrolysis from an ion like $SbCl_6^-$ to an ion of the type $SbCl_x(OH)_{6-x}^-$ as the hydrochloric acid concentration is decreased from *ca.* 11 *F* to 3.5 *F*.

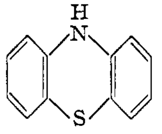
PASADENA, CALIF. RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

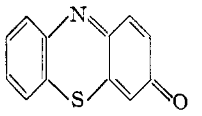
Phenothiazine Derivatives: Mono-oxygenated Compounds

BY DAVID F. HOUSTON, E. B. KESTER AND FLOYD DEEDS

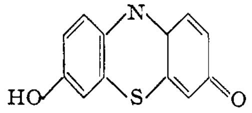
Phenothiazine (I) has been shown[2] to have *in vitro* tuberculostatic action which is somewhat diminished in the presence of serum. The oxidized derivatives known as phenothiazone (II) and thionol (III) also showed a moderate inhibiting effect, and it was postulated that their lesser effectiveness might be connected with their decreased solubility in lipids. Compounds having substituents on the nitrogen were relatively ineffective, suggesting that the nitrogen should be free to take part in oxidation–reduction effects.



(I)



(II)



(III)

The indications are, therefore, that compounds related to phenothiazine and thionol which have unsubstituted nitrogen atoms and increased lipid solubilities might show greater tuberculostatic action. A number of compounds meeting these requirements have been synthesized, and this paper reports a series of ethers related to phenothiazone.[3]

Phenothiazone-3 was first prepared as a noncrystalline compound by Bernthsen[4] by fusion of *p*-hydroxydiphenylamine with two atoms of sulfur, recovery as 3-hydroxyphenothiazine, and oxidation with ferric chloride. Kehrmann[5] later obtained it as a crystalline product, melting at 165–166°, by ferric chloride oxidation of phenothiazine in hot aqueous alcohol. A convenient modification of this method by Pummerer and Gassner[6] gave a product melting at 162–163°. A reported improvement of this process is the subject of a recent patent.[7] The crude product is recrystallized and 45% of phenothiazone-3 melting at 163–164° is obtained. Similarly, Granick, Michaelis and Schubert[8] recrystallized the product from the reaction and found a melting point of 161°. Small-scale experiments in this Laboratory have given yields up to 62.5%, though the reaction was very susceptible to changes in process conditions.

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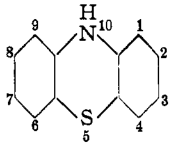
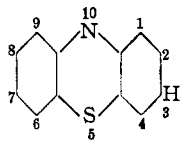
[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted. Presented at A. C. S. meeting, San Francisco, California, March 27–April 1, 1949.

[2] B. L. Friedlander, *Proc. Soc. Exptl. Biol. Med.*, **57**, 106–107 (1944).

[3] The awkwardness in naming derivatives of phenothiazine and related compounds has been pointed out by Michaelis and co-workers [THIS JOURNAL, **62**, 1802 (1940), and **63**, 351 (1941)], who also emphasized that the difficulties were greater with the quinonimine or oxidized form than with the hydroxyamine or reduced form. This trouble is largely overcome, however, by basing names of reduced-from compounds on the phenothiazine skeleton A (Ring Index No. 1860) and those of oxidized-form compounds on the theoretical 3-isophenothiazine skeleton B (Ring Index No. 1859).



(A)



(B)

Although this has the disadvantage of naming the reduced and oxidized forms of a compound on the basis of two isomeric ring skeletons, it offers a systematic nomenclature for phenothiazine derivatives that conforms with the present usage of *Chemical Abstracts*. The disadvantage has been avoided, at least in part, in this paper by the common use of the term phenothiazine (Skeleton A) to denote the parent compound of derivatives of the reduced form, and phenothiazone-3 instead of 3-isophenothiazine-3-one (from Skeleton B) as the parent compound for derivatives of the oxidized form.

[4] A. Bernthsen, *Ann.*, **230**, 182 (1885); *Ber.*, **17**, 2860 (1884).

[5] F. Kehrmann, *Ann.*, **322**, 54 (1902).

[6] R. Pummerer and S. Gassner, *Ber.*, **46**, 2324 (1913).

[7] Nederlandische Centrale Organisatie voor Toegepast Natuurwetenschappelijk Orderzoek, Dutch Patent 59,559, June 16, 1947, *C. A.*, **41**, 5557 (1947).

[8] S. Granick, L. Michaelis and M. P. Schubert, THIS JOURNAL, **62**, 1802 (1940).