Summary

1. The sorption of vapors of toluene and acetic acid by sugar carbon affords saturation values nearly independent of the absolute temperature.

2. Determination of the true sorption of both solvent and solute is in accordance with the conception that toluene and acetic acid can replace each other in the adsorbed film.

3. These absolute determinations of sorption agree with the ordinary relative determinations which exhibit "positive sorption" of acetic acid.

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THE ELECTROMETRIC TITRATION OF ANTIMONY AND TIN BY POTASSIUM DICHROMATE

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Received August 19, 1924 Published December 13, 1924

The quantitative oxidation of antimony in a hydrochloric acid solution from the trivalent to the pentavalent state by a standard solution of potassium dichromate has been observed by Kessler[1] and that of tin from the bivalent to the quadrivalent condition by Steng.[2] In each of these methods difficulty was experienced in observing the end-point of the titration. Recently an oxidimetric study of antimony has been made by Knop.[3] Since the work of Hildebrand[4] a large amount of investigation has been made in the application of the electrometric indicator in volumetric analysis. In the present study the estimations of antimony and tin have been made using an oxidation-reduction electrode. Antimonous and stannous chlorides were titrated in a hydrochloric acid solution singly and in mixtures by potassium dichromate. By adding an excess of mercuric chloride to a mixture of the two before titration, the tin is oxidized and the antimony content is accurately determined in the presence of the tin. The mercurous and mercuric chlorides present in the cell exert no influence on the character of the titration.

Apparatus and Materials

The apparatus used was the same as that described by Hildebrand[4] except that the hydrogen electrode was replaced by one of platinum foil and the mercury electrometer by a Leeds and Northrup portable galvanometer. A normal calomel electrode served as the constant half of the cell, the other half of which was a 200cc. beaker containing the solution to be titrated and into which dipped the platinum electrode.

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[1] Kessler, *Pogg. Ann.*, **118**, 17 (1863).

[2] Steng, *ibid.*, **92**, 57 (1854).

[3] Knop, *Z. anal. Chem.*, **63**, 81 (1923).

[4] Hildebrand, This Journal, **35**, 869 (1913).

Solutions of potassium dichromate, antimonous and stannous chlorides were prepared and analyzed. The stannous chloride solution was prepared by dissolving pure tin in hydrochloric acid and was preserved and measured out in an atmosphere of carbon dioxide. The antimonous chloride solution was prepared by dissolving pure antimonous oxide in dil. hydrochloric acid. It was carefully preserved so that the oxidizing influence of atmospheric oxygen was reduced to a minimum. The normalities of the stannous and antimonous chloride solutions were fixed by titration with a solution of potassium dichromate which in turn was titrated against pure Mohr's salt. The electrometric indicator was used throughout. The dichromate solution was 0.1 *N*, the stannous chloride 0.2020 *N* and the antimonous chloride 0.09893 *N*. Freshly boiled, distilled water was used in preparing and diluting the solutions.

The Titrations

All titrations were carried out at room temperature and the mixtures were constantly stirred. The initial volumes in all cases were 100 cc. and the hydrochloric acid content 15 cc. (d. 1.18) per 100 cc. The titration curves were plotted as voltage observed against cubic centimeters of dichromate added.

Five titrations were made of 5.00 cc. of the stannous chloride solution which was found to be equivalent to 10.10 cc. of 0.1 *N* dichromate, as calculated. The change in the voltage at the end of the titration is very large, from —100 to +600 mv., as was observed by Hostetter and Roberts.[5]

Five titrations were made of 9.40 cc. of the antimonous chloride solution which was found to be equivalent to 9.30 cc. of 0.1 *N* dichromate, as calculated. The rise in voltage at the end of this titration amounts to 80–100 mv.

Various proportions of stannous and antimonous chlorides were then taken and the mixture titrated. Table I contains the results.

Table I

Titration in Air of a Mixture of Stannous and Antimonous Chlorides

0.2020 *N* $SnCl_2$ taken Cc.	0.09893 *N* $SbCl_3$ taken Cc.	0.1 *N* dichromate required Cc.	0.1 *N* dichromate[a] taken	Error %
5.00	9.40	19.40	19.30	0.51
5.00	9.40	19.40	19.35	.25
2.50	9.40	14.35	14.30	.35
2.50	9.40	14.35	14.35	..
5.00	5.05	15.10	15.10	..

[a] These numbers are significant to ±0.025 cc.

The slight errors denoted were caused by air oxidation; such titration should always be carried out in an inert atmosphere such as one of nitro-

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[5] Hostetter and Roberts, This Journal, **41,** 1337 (1919).

gen or carbon dioxide. The titration curves of the mixtures have the same appearance as those obtained where only stannous chloride is titrated.

The next step consisted in taking various proportions of stannous and antimonous chlorides and then adding an excess of solid mercuric chloride immediately before titration. The titration curves obtained are those typical of antimonous chloride. The presence of mercury salts is seemingly without effect. The results are given in Table II.

TABLE II

TITRATION OF ANTIMONOUS CHLORIDE IN THE PRESENCE OF STANNOUS CHLORIDE AFTER THE ADDITION OF MERCURIC CHLORIDE IN EXCESS

The quantities of stannous and antimonous chlorides used were the same as in the experiments of Table I

0.1 *N* Dichromate required, cc.	9.30	9.30	9.30	9.30	5.00
0.1 *N* Dichromate[a] taken, cc.	9.25	9.30	9.30	9.30	5.00
Error, %	0.5	0.0	0.0	0.0	0.0

[a] These numbers are significant to ±0.025 cc.

The relative absence of errors in these titrations bears out the suggestion that the errors in titrating the mixtures were caused by slight oxidation of the stannous chloride during titration.

When arsenious chloride is substituted for the antimonous chloride in these titrations, analogous results are obtained.

The writer wishes to extend his thanks to Dr. Herbert S. Harned at whose suggestion these experiments were undertaken.

Summary

1. Stannous and antimonous chlorides may be titrated by potassium dichromate in a hydrochloric acid solution using the oxidation-reduction electrode as the indicator of the end-point.

2. Both may be titrated together in one sample.

3. The antimony can be titrated in presence of the tin after the addition of an excess of mercuric chloride.

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