[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polarographic Characteristics of Stannous and Cupric Tartrate Complexes and Amperometric Titration of Tin with Cupric Ion in Tartrate Medium

BY JAMES J. LINGANE

Recently, incidental to a study of amperometric titrations with titanous solutions, Strubl[1] mentioned that the stannous tartrate complex ion produces an anodic wave in a saturated tartaric acid supporting electrolyte, but he did not supply further details. Since this anodic wave should have considerable value in connection with the polarographic determination of tin in the presence of other metallic elements with which it is commonly associated, the present investigation was undertaken to obtain more complete information about the polarographic characteristics of the stannous and stannic complexes present in various tartrate media.

An amperometric titration of stannous tin with cupric ion in tartrate medium is also described.

Experimental

The usual polarographic technique was employed, a calibrated Sargent–Heyrovsky Polarograph being used to record polarograms.[2] The dropping mercury electrode was of the type described by Lingane and Laitinen,[3] and the rate of flow of mercury was determined and checked at frequent intervals by means of the volumetric instrument already described.[4] An H-type cell[2,3] was used, with either a saturated calomel or mercury–mercurous sulfate electrode as a working reference electrode. All measurements were performed with the cell in a water thermostat at 25.00°, and air was removed from the solutions with purified nitrogen.

Standard solutions of stannous chloride in 0.1 *N* hydrochloric or perchloric acid were freshly prepared as needed; they were standardized and checked at each time of use by pipetting samples under an excess of acidified ferric sulfate solution and titrating with standard ceric solution with *o*-phenanthroline ferrous complex as indicator. To avoid air-oxidation of the stannous tartrate complex, the solutions investigated were made up in the cell, the stannous chloride solution being added last after air had been removed from the supporting electrolyte solution with nitrogen. The *p*H values of the tartrate solutions were determined with a glass electrode circuit.

Behavior of the Stannous Tartrate Complex.—Polarograms of a relatively dilute solution of +2 tin in 0.5 *M* sodium potassium tartrate, with and without gelatin present, are shown in Fig. 1. Cathodic current (reduction) is indicated by a positive sign and anodic current (oxidation) by a negative sign. It will be noted that the cathodic and anodic waves of curve *a* (without gelatin) both include prominent maxima, but very well-defined diffusion currents are obtained following the maxima. Both maxima are completely eliminated by the addition of a small amount of gelatin (0.006%), as shown by curve *b*. Since there is no doubt that the cathodic wave corresponds to the reduction of the stannous tartrate complex to the metallic state, and since the cathodic and anodic diffusion currents are equal (see also Table II), it is evident that the anodic wave results from the oxidation of the stannous tartrate complex to the stannic state.

The character of the polarograms is remarkably different in acidic and alkaline tartrate supporting electrolytes, as shown in Fig. 2. From the curves in Fig. 2, and the summary of half-wave potential data in Table I, it is seen that the cathodic and anodic half-wave potentials are both shifted to much more negative values in going from acidic to alkaline tartrate media. This marked *p*H effect indicates that there is a fundamental difference in the composition of the stannous complex in acidic and alkaline tartrate solutions. In acidic tartrate medium an *acido* complex, *i. e.* containing coördinated hydrogen tartrate ion or tartaric acid molecules, probably predominates.

TABLE I

HALF-WAVE POTENTIALS OF STANNOUS TIN IN TARTRATE MEDIUM AS A FUNCTION OF *p*H

The concentration of stannous tartrate complex was 5.45 × 10^{-3} *M* in all cases, and 0.01% gelatin was present as a maximum suppressor. The values of the half-wave potentials are referred to the saturated calomel electrode at 25°.

Supporting electrolyte, molar					$E_{1/2}$, volts	
$H_2C_4H_4O_6$	$NaHC_4H_4O_6$	$Na_2C_4H_4O_6$	Other salts	*p*H	an.	ca.
0.40	0.10			2.3[a]	−0.14	−0.49
	.38	0.047	0.38 NaCl	3.4[a]	.20	.54
	.11	.36	.11 $NaClO_4$	4.3[a]	.28	.59
		.43	.10 $NaClO_4$	9.0[b]	.33	.92
		.43	.0017 NaOH	9.8[a]	.34	.95
		.47	.10 NaOH	13.0[c]	.71	1.16
		.48	.2 NaOH	13.3[c]	.77	1.18

[a] Measured with glass electrode. [b] From transition color of thymol blue. [c] Calculated from concentration of sodium hydroxide.

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(1) R. Strubl, *Coll. Czechoslov. Chem. Commun.*, **10**, 490 (1938).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(3) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(4) J. J. Lingane, *ibid.*, **14**, 655 (1942).

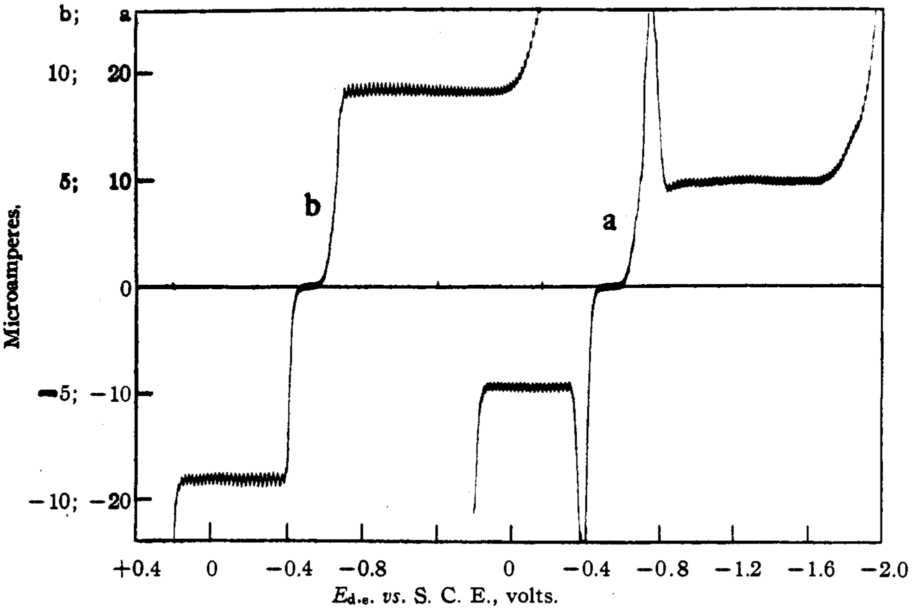

Fig. 1. (a)—Polarogram of 1.62×10^{-3} *M* stannous tin in 0.5 *M* sodium potassium tartrate; (b) 0.006% gelatin added; galvanometer sensitivity twice as great for curve b as for curve a.

In strongly alkaline medium a part of the coordinating tartrate ion is probably replaced by hydroxyl ion to form a basic *hydroxo-tartrato* complex. At intermediate *p*H values mixtures of various species appear to be present. Evidence for this latter conclusion is found in the fact that at a *p*H of about 9 a small inflection, suggestive of a double wave, is observed in the cathodic wave (see curve *b* in Fig. 2), which signifies the presence of two different complexes in sluggish equilibrium with each other.

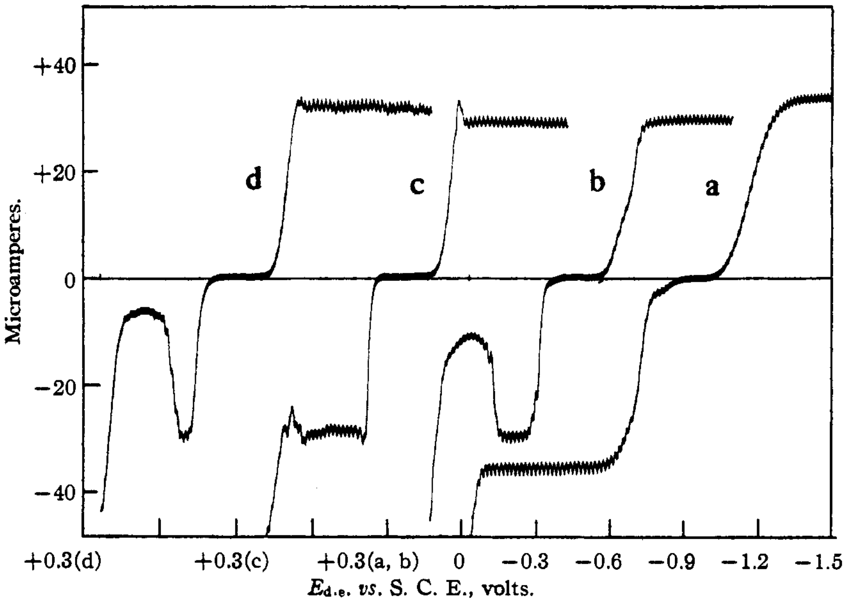

Fig. 2.—Polarograms of the stannous tartrate complex in acid, neutral and alkaline tartrate media. 5.45×10^{-3} *M* Sn^{+2} in all cases, and 0.01% gelatin was present as a maximum suppressor. Compositions of the supporting electrolytes were: (a) 0.5 *M* disodium tartrate plus 0.1 *N* sodium hydroxide; (b) 0.5 *M* disodium tartrate plus 0.1 *N* sodium chloride (solution *a* neutralized with hydrochloric acid to *p*H 8–9); (c) 0.047 *M* disodium tartrate, 0.38 *M* sodium hydrogen tartrate, and 0.38 *M* sodium chloride (*p*H 3.4); (d) 0.40 *M* tartaric acid plus 0.1 *M* sodium hydrogen tartrate (*p*H 2.3).

The anodic half-wave potential shifts to a more positive value with increasing concentration of the stannous tartrate complex. For example, with a supporting electrolyte of *p*H 4.3, composed of 0.38 *M* disodium tartrate, 0.12 *M* sodium hydrogen tartrate, and 0.01% gelatin, the anodic half-wave potentials of 1.88, 3.68, 5.45, and 7.08 millimolar stannous tartrate were, respectively, −0.35, −0.31, −0.28 and −0.27 v. *vs.* the saturated calomel electrode (see Fig. 3). On the other hand, the cathodic half-wave potential in the above experiments remained constant at −0.60 ± 0.01 v. These results indicate that the oxidation of the stannous tartrate complex is thermodynamically irreversible at the dropping electrode. The irreversibility was confirmed by investigating polarograms of *stannic* tin in tartrate media. In neutral or alkaline tartrate solutions stannic tin does not show a reduction wave below the potential at which sodium ion is discharged, whereas if the stannous-stannic system were reversible a reduction wave would be observed with stannic tartrate solutions at the same potential at which the anodic wave occurs with stannous tartrate solutions.

Judging from the slope of the cathodic wave, the reduction of the stannous tartrate complex is also irreversible at the dropping electrode, but much less so than the oxidation process.

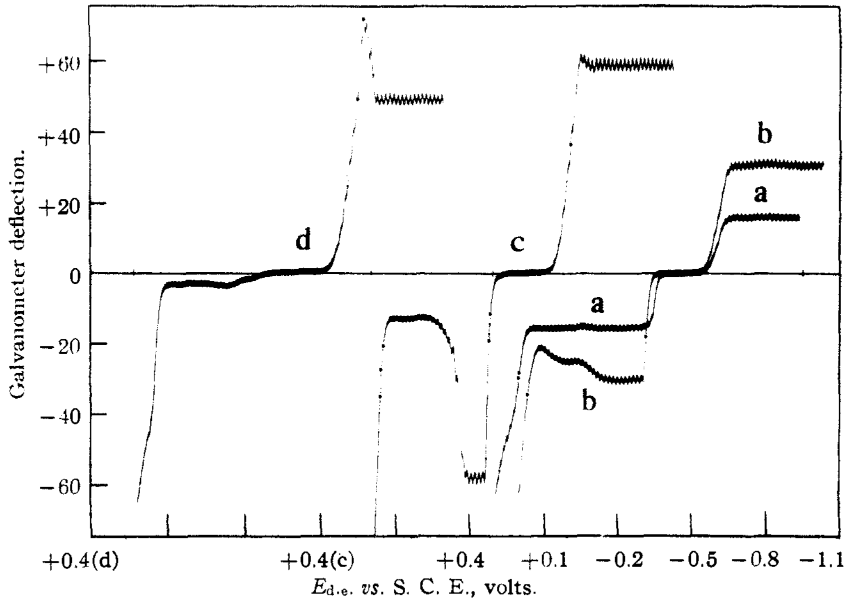

Fig. 3.—Various concentrations of stannous tin in 0.38 *M* disodium tartrate, 0.12 *M* sodium hydrogen tartrate, and 0.01% gelatin. Concentrations of tin were (a) 1.88, (b) 3.68, (c) 7.08, and (d) 14.6 millimolar. Galvanometer sensitivity was 0.670 microamp. per mm. for curves a, b and c; 1.675 microamp. per mm. for curve d.

In acidic tartrate solutions the anodic wave is characterized by a remarkably steep slope; by manual manipulation of the polarograph it was found that a change of only 5 or 6 millivolts in the vicinity of the half-wave potential caused the anodic current to drop from its limiting value to practically zero. This indicates that whatever the slow step in the oxidation process may be it requires a very sharply limited activation energy.

It is seen from the curves in Fig. 2 that the character of the anodic diffusion current differs markedly in acid and alkaline tartrate solutions. In alkaline tartrate medium (curve *a* in Fig. 2) the anodic diffusion current is excellently defined and quite normal. At a *p*H of about 8–9, corresponding approximately to the *p*H of a pure solution of disodium tartrate (curve *b*), the anodic diffusion current is somewhat smaller than in the strongly alkaline medium; this is easily explicable by a change in the nature of the tartrate complex (*vide supra*) with a corresponding change in diffusion coefficient. However, it will be noted that the anodic diffusion current in curve *b* decreases abruptly prior to the anodic dissolution current of the mercury, so that a pronounced minimum occurs in the curve. This minimum is even more evident in a tartaric acid–sodium hydrogen tartrate supporting electrolyte (curve *d* in Fig. 2). The minimum is only slightly noticeable in curve *c* of Fig. 2; probably because of the relatively large concentration of chloride ion (0.38 *M*) present in this solution, which depolarizes the dropping electrode at a potential more negative than that at which the minimum is fully developed.

Similar, although less prominent, minima have been observed in the anodic waves of hydroquinone[5] and of reduced rhenium solutions.[6] Hence the present case is not unique, and the occurrence of such a minimum does not appear to be simply related to the type of substance that is oxidized at the dropping electrode. Since the decrease in current causing the minimum occurs near the potential at which oxidation of the mercury of the dropping electrode begins, apparently the oxidation of the mercury inhibits the oxidation of other substances. It is significant that the minimum is much less prominent in the presence of a high concentration of chloride ion, and completely absent in the presence of hydroxyl ion (curves *c* and *a* in Fig. 2), in which cases the dropping electrode is depolarized at a relatively positive potential and the products of the oxidation of the mercury are mercurous chlo-

(5) O. H. Müller and J. P. Baumberger, *Trans. Am. Electrochem. Soc.*, **71**, 169, 181 (1937).

(6) J. J. Lingane, This Journal, **64**, 2182 (1942).

ride and mercuric oxide, respectively, rather than free mercurous ion. The minimum is not caused by the gelatin present as a maximum suppressor, and it was equally pronounced in the absence of gelatin.

The minimum does not occur when the concentration of stannous tartrate complex is smaller than about 2 × 10^{-3} *M*, but it appears and becomes increasingly pronounced at larger concentrations. This is demonstrated by the polarograms in Fig. 3 of various concentrations of stannous tin in an acidic tartrate supporting electrolyte. When the concentration of tin exceeds about 0.01 *M* the entire anodic wave practically disappears (curve *d* in Fig. 3).

The data in Table II demonstrate the equality of the anodic and cathodic diffusion currents and their linear proportionality to the concentration of the stannous tartrate complex. It will be noted that the anodic diffusion current at −0.2 v. is strictly proportional to the concentration of the stannous complex even with concentrations which produce minima in the anodic waves. Hence the occurrence of the minima will not interfere seriously with practical analytical applications of the anodic wave, provided that the concentration of tin does not exceed about 0.007 *M* so that a diffusion current is obtained before the minimum starts.

By introducing the values of $m^{2/3}t^{1/6}$ and i_d/C from Table II into the Ilkovic equation,[2] the diffusion coefficient of the stannous tartrate complex is calculated to be 0.40 × 10^{-5} cm.^{2} sec.$^{-1}$ in this particular acidic tartrate supporting electrolyte at 25°. With an alkaline tartrate supporting electrolyte, composed of 0.5 *M* disodium tartrate, 0.1 *N* sodium hydroxide, and 0.01% gelatin, and the same capillary used to obtain the data in Table II, the value of i_d/C was found to be 6.63 microamp. per millimole per liter, from which the diffusion coefficient is calculated to be 0.56 × 10^{-5} cm.^{2} sec.$^{-1}$ at 25°. This considerably larger value of the diffusion coefficient in alkaline medium is further evidence that part of the coördinating tartrate ion is replaced by hydroxyl ion to form a *hydroxo-tartrato* stannous complex ion, with a consequent decrease in ion size.

TABLE II

DIFFUSION CURRENTS OF THE TARTRATO STANNOUS COMPLEX AS A FUNCTION OF CONCENTRATION

Supporting electrolyte composed of 0.4 *M* disodium tartrate, 0.1 *M* sodium hydrogen tartrate, 0.1 *M* sodium chloride, and 0.01% gelatin (*p*H = *ca.* 4.5). Anodic diffusion current measured at −0.2 v. and cathodic diffusion current measured at −0.8 v. *vs.* the S. C. E. The values given have been corrected for the residual currents: −0.005 microamp. at −0.2 v., and +0.19 microamp. at −0.8 v. Temp. = 25.00°. $m^{2/3}t^{1/6}$ = 2.32 mg.$^{2/3}$ sec.$^{-1/2}$.

Sn^{+2} millimolar	i_d, microamp. Anodic	i_d, microamp. Cathodic	i_d/C, microamp./mmole/l. Anodic	i_d/C, microamp./mmole/l. Cathodic
0.170	−0.98		5.76	
1.88	10.6	10.5	5.64	5.59
1.93	11.0	10.9	5.71	5.66
3.68	20.6	20.5	5.61	5.58
4.12	23.2	23.0	5.63	5.58
5.42	30.2	30.3	5.58	5.60
7.08	39.2	39.3	5.54	5.56
14.6	[a]	82.6	[a]	5.66
			Av. 5.64 ± 6	5.61 ± 4

[a] Anodic wave practically absent; see curve *d*, Fig. 3

Behavior of Copper in Tartrate Media.—The cupric tartrate complex present in *acidic* tartrate media is reduced at the dropping electrode to produce a well-defined wave, as shown by curve *a* in Fig. 4, and the magnitude of the diffusion current corresponds to complete reduction to the metallic state.[7] In a supporting electrolyte composed of 0.38 *M* disodium tartrate, 0.12 *M* sodium hydrogen tartrate, and 0.01% gelatin (*p*H 4.3) the half-wave potential is −0.086 v. *vs.* the S. C. E. (curve *a* in Fig. 4). A good wave, with $E_{1/2}$ = −0.118 v., is also obtained in 0.5

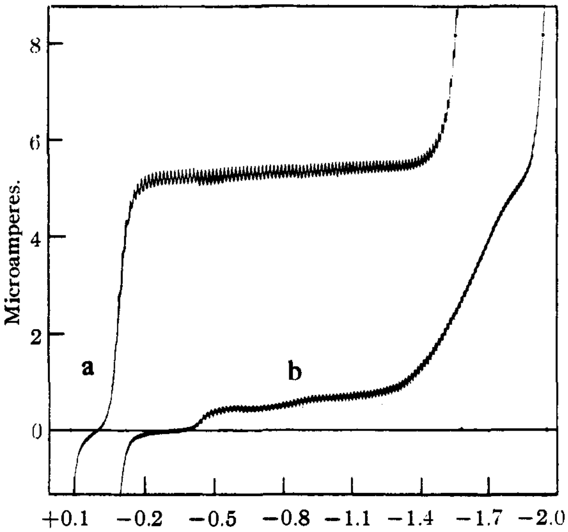

Fig. 4.—Polarograms of cupric tartrate complex in acidic and alkaline tartrate media. (a) 1.03 × 10^{-3} *M* copper in 0.4 *M* disodium tartrate, 0.1 *M* sodium hydrogen tartrate, 0.1 *N* sodium chloride, and 0.01% gelatin (*p*H ~ 4.5). (b) 1.03 × 10^{-3} *M* copper in 0.5 *M* disodium tartrate, 0.1 *N* sodium hydroxide and 0.01% gelatin.

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(7) See also K. Suchy, *Coll. Czechoslov. Chem. Commun.*, **3**, 354 (1931).

M disodium tartrate (*p*H~9). In a strongly alkaline tartrate solution, the wave is shifted to such a negative potential (−1.6 v.) that it is practically completely masked by the discharge of sodium ion, as shown by curve *b* in Fig. 4, and a small "pre-wave" is also observed starting at about −0.4 v. The character of curve *b* suggests that there are two species of cupric tartrate complex present in the alkaline solution in sluggish equilibrium with each other; the predominating and more difficultly reducible of the two is probably a basic *hydroxo-tartrato* complex, and the other, which produces the small wave at −0.4 v., is probably the same complex that is present in the neutral and slightly acid tartrate solutions.

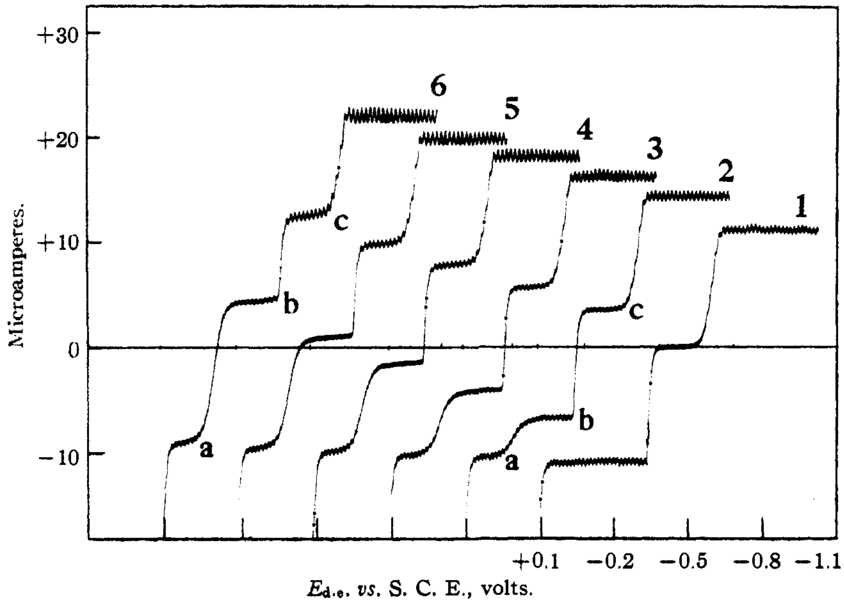

Fig. 5.—Amperometric titration of stannous tartrate complex with cupric ion: 55.0 cc. of 1.93 × 10^{-3} *M* stannous tin in 0.38 *M* disodium tartrate, 0.12 *M* sodium hydrogen tartrate, 0.12 *M* sodium chloride, and 0.01% gelatin (*p*H 4.3) plus (1) 0, (2) 3.00, (3) 5.00, (4) 7.00, (5) 9.00, and (6) 12.00 cc. 0.0130 *M* cupric sulfate from a microburet. Equivalent volume of cupric sulfate = 8.19 cc. Nitrogen bubbled through solution for three to four minutes after each addition of cupric sulfate solution. Each curve starts at $E_{d.e.}$ = +0.1 v.

In a supporting electrolyte composed of 0.4 *M* disodium tartrate, 0.1 *M* sodium hydrogen tartrate, and 0.01% gelatin the diffusion current constant of the cupric complex was found to be equal to 5.50 ± 0.05 microamp./millimole/liter at −0.2 v. at 25° with $m^{2/3}t^{1/6}$ = 2.32 mg.$^{2/3}$ sec.$^{-1/2}$. The corresponding diffusion coefficient, 0.385 × 10^{-5} cm.^{2} sec.$^{-1}$, is only slightly smaller than that of the stannous complex.

Amperometric Titration of Tin with Cupric Ion in Tartrate Medium. Since the half-wave potential for the reduction of Cu^{+2} in acidic tartrate media is in the vicinity of −0.1 v. and that for the oxidation of Sn^{+2} is about −0.3 v., and bearing in mind that the reversible potential of the stannous–stannic tartrate system is actually more negative (greater reducing power) than the above half-wave potential indicates, because the oxidation is irreversible at the dropping electrode, one would predict that +2 copper would be completely reduced to the metallic state by +2 tin in acidic tartrate medium. Actually we found that this reaction does not occur with measurable speed at room temperature, and apparently it requires a large activation energy. However, even though there is no reaction in the bulk of the solution, it is still possible to titrate accurately +2 tin in tartrate medium with a cupric salt solution by taking advantage of the fact that in the potential range from −0.1 to −0.3 v. the cathodic diffusion current of copper *compensates* the anodic diffusion current of the tin. The general principles underlying this type of titration have been discussed recently by Kolthoff and Miller.[8]

A typical set of polarograms obtained in such a titration, with analytical details supplied in the legend, is shown in Fig. 5. It is seen that the addition of cupric ion to the stannous tartrate solution causes the appearance of the cupric wave at −0.1 v., and as long as excess tin is present (curves 2, 3, and 4) this *cathodic* cupric wave actually appears on the *anodic* portion of the polarograms. Since both the height of the cathodic wave of the tin at −0.6 v. and the anodic diffusion current of the tin between +0.1 v. and −0.1 v. remain constant (after allowance for the increase in volume during the titration), it is quite evident that *there is no direct reaction between the cupric and stannous complexes in the body of the solution.*

(8) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **62**, 2171 (1940); see also ref. 2, p. 210.

The titration curve (net current at −0.2 v. *vs.* volume of cupric solution) is strictly linear, and the end-point can be determined precisely even with stannous solutions as dilute as 10^{-4} M when proper correction is made for the residual current. The end-point occurs when the net current at −0.2 v. becomes equal to the residual current of the supporting electrolyte, or equal to zero after correction for the residual current. This end-point is not exactly coincident with the equivalence point (corresponding to a solution containing equimolar concentrations of copper and tin) because the diffusion coefficients, and hence diffusion current constants, of the stannous and cupric tartrate complexes are not identical. At the end-point

$$\left(\frac{C_{\text{Cu}}}{C_{\text{Sn}}}\right)_{i=0} = \frac{k_{\text{Sn}}}{k_{\text{Cu}}} = \left(\frac{D_{\text{Sn}}}{D_{\text{Cu}}}\right)^{1/2} \qquad (1)$$

where the D's are the diffusion coefficients of the two complexes, and the k's are their diffusion current constants.

From the previously determined values of k_{Sn} and k_{Cu} the ratio $C_{\text{Cu}}/C_{\text{Sn}}$ at the end-point should be equal to 5.62/5.50 or 1.02 ± 0.01. Since the accuracy of the directly determined diffusion current constants is not better than about ±1%, several titrations of various concentrations of tin were performed to determine the above ratio more precisely. The results obtained are recorded in Table III.

TABLE III

SUMMARY OF AMPEROMETRIC TITRATIONS OF VARIOUS CONCENTRATIONS OF TIN

Supporting electrolyte and titration technique as in Fig. 5. Initial volume of stannous tartrate solution was 50 cc. in all cases. Concentrations of the cupric sulfate titrating solution adjusted so that 5 to 8 cc. were required to reach the end-point, and volumes were measured with a microburet with a precision of ±0.2%.

Sn^{+2}, millimoles per 50 cc.	Cu^{+2}, millimoles required	$C_{\text{Cu}}/C_{\text{Sn}}$ at $i = 0$
0.00934	0.00955	1.022
.0543	.0553	1.018
.1063	.1062	0.999
.1969	.1930	.982
.2060	.1993	.969

With the two most dilute stannous solutions the ratio $C_{\text{Cu}}/C_{\text{Sn}}$ agrees with the value predicted from the diffusion current constants, and the accuracy of the titration appears to be limited only by the accuracy of the current and volume measurements. However, with concentrations of tin greater than about 0.001 M (0.05 millimole or 6 mg. of Sn per 50 cc.) the ratio becomes increasingly smaller than the expected value. This critical concentration coincides with the concentration above which a minimum occurs in the anodic diffusion current of the tin, and hence it is evident that the same phenomenon which causes the minimum is also responsible for the abnormally small titration ratio. It is rather surprising, however, that the titration ratio should be influenced by the occurrence of the minimum, since the anodic diffusion current at −0.2 v. is not affected (see Table II). Because of this effect practical applications of this titration will be limited to small concentrations of tin (less than about 10 mg. per 50 cc.) but in such cases it may prove to be of considerable utility.

Summary

Polarograms of the stannous tartrate complex in tartrate media comprise cathodic and anodic waves of equal height; the cathodic wave corresponds to reduction to the metallic state and the anodic wave results from oxidation of the stannous complex to the stannic state. Both diffusion currents are directly proportional to the concentration of the stannous complex. In acidic tartrate media a minimum occurs in the anodic diffusion current when the concentration of tin exceeds about 0.002 M, and with concentrations larger than about 0.01 M the anodic wave practically disappears. Data are given for the half-wave potentials of both waves as a function of the pH of the tartrate supporting electrolyte. The cathodic half-wave potential is independent of the concentration of the stannous complex, but in acidic tartrate media the anodic half-wave potential shifts to a more positive value with increasing concentration. The cathodic and anodic reactions are both irreversible at the dropping electrode, the latter more so than the former.

In acidic tartrate medium the cupric tartrate complex produces a very well-defined cathodic wave, but in alkaline tartrate solutions the wave is shifted to such a negative potential that it is practically completely masked by the discharge of sodium ion from the supporting electrolyte. A small pre-wave was also observed in alkaline tartrate medium.

An amperometric titration of stannous tin with cupric ion in a tartrate supporting electrolyte is described, which is based on a compensation

of the anodic diffusion current of tin by the cathodic diffusion current of copper without direct reaction in the body of the solution.

CAMBRIDGE, MASS. RECEIVED JANUARY 4, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Red Zinc Oxide[1]

BY WILLIAM EHRET AND ARTHUR GREENSTONE

The physical properties of zinc oxide cause it to be classed as a covalence compound with some electrovalence characteristics. It involves tetrahedral bonding and is a semi-conductor. In view of the labile state of the electrons associated with the last mentioned property, it is not surprising to find that the compound, when heated, absorbs energy in the visible region of the spectrum, thus appearing yellow. This is a reversible phenomenon as is well known; the color disappears upon cooling to room temperature. In the present paper will be described a substance which by ordinary standards of analysis would pass for pure zinc oxide and which possesses a permanent[2] red[3] color at room temperature. This color is lost upon heating at 300° and above and it does not return upon cooling. The present report will be concerned chiefly with the methods of preparation, the composition, some of the properties and the possible causes of the color of the material.

Red zinc oxide has been described in a cursory way by some previous workers. The mineral zincite is often found with a red tint and its color has been ascribed to impurities, chiefly manganese and iron.[3a] Mylius and Fromm[4] observed the formation of red zinc oxide when the hydrolytic products of an ammoniacal zinc nitrate solution were heated. Kutzelnigg[5] prepared it by heating mixtures of zinc oxide and ammonium nitrate to the point of deflagration. He suggested that the color might be due to a nitrogen compound since his red zinc oxide contained nitrogen in an "oxidized" form which he reported as 0.25% nitrogen pentoxide.

Preparation

Fusion of Zinc Oxide and Ammonium Nitrate.—Red zinc oxide was prepared for most of our experiments according to the method outlined by Kutzelnigg. The various factors which influence the preparation of the substance by this method were carefully studied in the hope of finding clues that might lead to an explanation of the color. Highly purified white zinc oxide, made by the method of Hüttig[6] (thermal decomposition of zinc oxalate) and used as a standard of reference throughout this work, was mixed with thrice recrystallized C. P. ammonium nitrate in 25 × 200 mm. Pyrex glass tubes. About 15 g. of the mixture was usually taken. The temperature was raised until a sudden deflagration spattered the contents of the tube up along its walls. The contents of the tube were then washed into a casserole where, by elutriation with successive portions of water totalling two liters. residual ammonium nitrate and white zinc oxide were removed. The fact that red zinc oxide sinks faster than white when in water suspension permitted separation of these two. The yield of red zinc oxide was approximately 50% of the white taken. It is believed that the white zinc oxide. always found admixed with the red. was present because frothing carried some of the mixture up along the walls of the tube where it escaped the final vigorous action which brought on the red color. Some of the original mixtures also probably contained more white zinc oxide than was consumed in the reaction mechanism.

Extensive tests showed that the rate of heating of the original material could be varied within wide limits without detectable influence upon the composition of the red zinc oxide formed. Some experiments involved a uniform rate of heating over a period of two and one-half hours to the point of deflagration, others one and one-half hours. and still others ten minutes. Further. it was found that substitution of C. P. zinc oxide for the highly purified form caused no analytically detectable difference in the final product. Time-heating curves were plotted for the mixtures. using a tube filled with sodium chloride as a control. These were reproducible to within 0.5% as judged by the time required to reach a given temperature. The thermal behavior of the mixtures was thus highly reproducible.

The heating curves usually exhibited a pronounced halt around 100°, which is just above one of the transition temperatures for ammonium nitrate. Evolution of am-

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(1) This paper is based on a dissertation presented by Arthur Greenstone in partial fulfillment of the requirements for the degree of Doctor of Philosophy. February, 1942.

(2) Ten years' exposure to ordinary light and atmosphere has produced no change in color. Similarly, two years' exposure to the weather in a paint has produced no change.

(3) The color, as determined by comparison with the Munsell color standards in accordance with the method of Judd and Kelly, *U. S. Bureau of Standards Research Paper* **1239**, Vol. 23, Sept., 1939 is, *weak reddish-orange*.

(3a) Dittler, *Z. anorg. allgem. Chem.*, **148**, 332 (1925).

(4) Mylius and Fromm, *ibid.*, **9**, 155 (1895).

(5) Kutzelnigg, *ibid.*, **208**, 23 (1932); **221**, 46 (1934)

(6) Hüttig, *Kolloid Beihefte*, **39**, 286 (1934).