The Complex-forming Behaviour of Tin, Germanium, and Titanium with Some Dibasic Carboxylic Acids.

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The conflicting reports of previous workers on complex formation between Sn(IV), Ge(IV), and Ti(IV) and tartaric acid have led to a re-examination of the problem, by electrometric, polarimetric, and polarographic methods.

Metal : tartrate combining ratios of 1 : 1 and 1 : 2, and possibly 1 : 4, are demonstrated for tin; 1 : 1, 1 : 2, and possibly 2 : 1 for germanium; and evidence is obtained of 2 : 1, 1 : 1, and 1 : 2 for titanium, although here many species (*e.g.*, polynuclear) may co-exist. The predominance of any complex depends on the conditions; the solutions are often colloidal. In this connection, the ageing properties of the complex solutions are described and discussed.

The complicating effects of hydrolysis restrict quantitative interpretation, particularly from electrometric measurements. These supply indications, however, that complex-forming characteristics of the three metals examined are the same in tartaric, malic, and succinic acid solutions.

A value for the concentration equilibrium constant between the chloro- and monotartrato-complexes of tin is calculated from polarographic data.

A SURVEY of the literature on the tartrate complexes of tin(IV) and titanium(IV), of importance in analytical chemistry, reveals several apparently conflicting results; and germanium(IV), which bridges the two metals in the sub-groups IVA and IVB of the Periodic Table, has only recently been studied in tartrate solutions (Vartapétian and Tchakirian, *Compt. rend.*, 1953, **236**, 81). These systems were therefore examined further to correlate existing data.

Earlier workers were chiefly concerned with attempts at isolation of complexes. Thus Henderson, Orr, and Whitehead (*J.*, 1899, **75**, 542) prepared substances of composition claimed to be $M^{IV}O(C_4H_4O_6M^I)_2,xH_2O$, where $M^{IV} = Sn^{IV}$ or Ti^{IV}, and M^I = Na, K, or NH_4.

Rosenheim and his co-workers (*Z. anorg. Chem.*, 1904, **39**, 170; 1901, **26**, 239) obtained products containing tin and tartrate combined in the ratio 1 : 1, and various gelatinous titanium compounds with titanium : tartrate ratios of 2:1, 2:3, and 1:2, the product obtained depending on the conditions. It is very doubtful whether these substances were homogeneous, however, in view of the preparative methods employed and the fact that extraction by alcohol frequently altered their composition. Other authors have expressed similar doubts in analogous circumstances (Dey, *J. Colloid. Sci.*, 1948, **3**, 472, and references therein); Dey has pointed out that these complex solutions are frequently colloidal, and so isolated products are liable to be indefinite. Dumanski and Kniga (*Kolloid-Z.*, 1928, **44**, 273) and Haïssinsky and Yang Jeng-Tsong (*Analyt. Chim. Acta*, 1949, **3**, 422) noted that solutions of high metal : tartrate ratio are colloidal, but ionic at higher tartrate concentrations (Dumanski and Kniga, *loc. cit.*).

In contrast to Rosenheim's conclusion of 1 : 1 combination (see above), Zolotukhin (*J. Gen. Chem., U.S.S.R.*, 1949, **19**, 983) has decided, from titration experiments, that 1 : 2 is the combining ratio between tin and tartrate. It may be noted that polarographic studies on the stannous–tartrate system (Lingane, *J. Amer. Chem. Soc.*, 1943, **65**, 866) were suggestive of the existence of two complexes in solution. The effects of dilution (Grossmann, *Ber.*, 1905, **38**, 711) and of hydrogen-ion concentration (Schenk, *Helv. Chim. Acta*, 1936, **19**, 639) on the titanium–tartrate system were examined polarimetrically, employing the 1 : 2 formulation, although Caglioti and Sartori (*Gazzetta*, 1936, **66**, 741) give the titanium : tartrate ratio as 2 : 3 in alkaline solution, and 1 : 1, shifting to 1 : 2 on dilution, in acid solution. Caglioti's work has been strongly criticised on theoretical grounds, however (Fouchay and Saucherre, *Bull. Soc. chim.*, 1947, 529).

The recent work of Vartapètian and Tchakirian (*loc. cit.*) on germanium(IV) oxide complexes with tartaric acid suggested 1 : 1 combination. Their investigations (published since completion of the present work) have been extended to a wider range of conditions, giving further information on the system (see below). This study used pH, polarimetric, and polarographic measurements.

EXPERIMENTAL

Much of the earlier work had apparently been vitiated by pre-reaction hydrolysis, so in order to enable the complex-forming ions to participate at least initially in competitive ionic equilibria, 4—5M-hydrochloric acid solutions were employed wherever practicable. Suitable adjustments to the acidity were made after the addition of complex-forming acid.

The tin used was in the form of ammonium hexachlorostannate, purified by double recrystallisation from a filtered solution in constant-boiling hydrochloric acid. It was used either as the solid (analysis for tin gave 99·88—100·0% of theoretical for various samples), or in 5N-" AnalaR " hydrochloric acid solution. A stock germanium solution was prepared by distilling germanium tetrachloride from spectrographically pure germanium dioxide in constant-boiling hydrochloric acid into similar acid, and standardised by the tannin method (Holness, *Analyt. Chim. Acta*, 1948, **2**, 254). Titanium was brought into solution by fusing the pure dioxide with potassium hydrogen sulphate and leaching the cooled melt with 3N-sulphuric acid. The titanium in the filtered solution was precipitated with ammonia, and the precipitate washed with 2% ammonium chloride solution and redissolved in 1 : 1 " AnalaR " hydrochloric acid, this procedure being repeated until the final solution was sulphate-free. Other materials used (tartaric and succinic acids, sodium hydroxide, and freshly-filtered ammonia) were all of " AnalaR " quality. The malic acid solutions were filtered before use to remove traces of insoluble matter.

The free acid content of titanium and germanium solutions could not be determined with any degree of accuracy, owing to hydrolysis and consequent liberation of acid brought about by addition of base in standardisation. An estimate was obtained by direct titration to the methyl-orange change with ammonia. This quantity, required in the polarimetric measurements, was adequately accurate, since in any given series the final acidity or alkalinity, calculated from the figure, was constant, so that the results in the series were comparable.

The commercial instruments used were a Cambridge Instrument Co. portable pH meter and glass electrode assembly (standardised by means of two buffer solutions of pH 4·00 and 9·20); a half-field polarimeter measuring to 0·01°, manufactured by Messrs. Bellingham and Stanley, Ltd. (the sodium-D lines were used as light source); and a Cambridge Instrument Co. pen-recording polarograph.

pH *Measurements.*—Titration experiments were carried out at a metal concentration of 10^{-3}M. Preliminary titrations with sodium hydroxide showed that the normal "additive" technique led to non-reproducibility, and consequently the "static" method was adopted, consisting in making up a series of solutions for a given titration curve, alkali content varying but the volume remaining constant. To the acid solution of the metal (suitably diluted immediately before use), the complexing acid was added, and diluted appropriately with water. After 2 min. from addition of acid, sodium hydroxide solution was added, to bring the total volume to 100 ml., and the glass electrode system inserted. The pH was measured after 4 min. from addition of acid; within 10 min. it was usually steady (see Results). Blank curves on the metal solution alone were obtained in a similar manner. All measurements were made at room temperature.

Polarimetric Measurements.—Job's method of continuous variations (*Ann. Chim.*, 1928, **9**, 113) was employed to determine the composition of the complexes formed, the enhanced optical rotatory power being used as a measure of complex formation. Behaviour at two total (metal + acid) concentration levels was investigated, $5{\cdot}0 \times 10^{-2}$M and 1·0M, except for germanium, where it was found not possible to prepare a stock chloride solution of sufficient concentration for a 1·0M-series. To the metal solution (or hexachlorostannate) varying quantities of freshly prepared (+)-tartaric acid solution were added, followed by water and ammonia solution to bring the final solution to a volume of 20 ml., and the desired acidity. All measurements were made at 20·0° ± 0·5°, this control being sufficient to prevent temperature variation errors. The tin and germanium solutions showed no variation in activity over a period of 30 min., during which time measurements could easily be effected. Titanium solutions required greater control, however (see Results).

Polarographic Measurements.—The cell used was a modification of the conventional low-resistance H-type, having a saturated calomel electrode as reference in one limb (Lingane and Laitinen, *Ind. Eng. Chem. Anal.*, 1939, **11**, 504). The cross-piece was set at an angle to the horizontal, to prevent streaming of the solutions in each limb owing to movement of the agar plug (Komyathy, Malloy, and Elving, *Analyt. Chem.*, 1952, **24**, 431); plug renewal was facilitated by incorporating a ground-glass joint. Electrical leakages into the earthed thermostat-bath water (all polarograms were recorded with the cell and contents at 25·00° ± 0·02°) were prevented by sealing the joint with vaseline.

Air was removed from the solutions investigated by passage for 20 min. of a stream of nitrogen, previously purified by bubbling through an alkaline solution of sodium dithionite (hydrosulphite) containing some sodium anthraquinone-β-sulphonate (Fieser's solution), and then through water.

Results

(I) *Tin.*—(a) pH *Measurements.* Despite close control, it was not possible to obtain a reproducible titration curve with a tin : tartrate ratio of 1 : 2, the complex solution being titrated against sodium hydroxide. Up to pH ~ 5·5, the curve was smooth, but in more alkaline conditions the pH varied erratically with time; *e.g.*, in 30 min. the pH of one solution rose from 8·15 to 8·46.

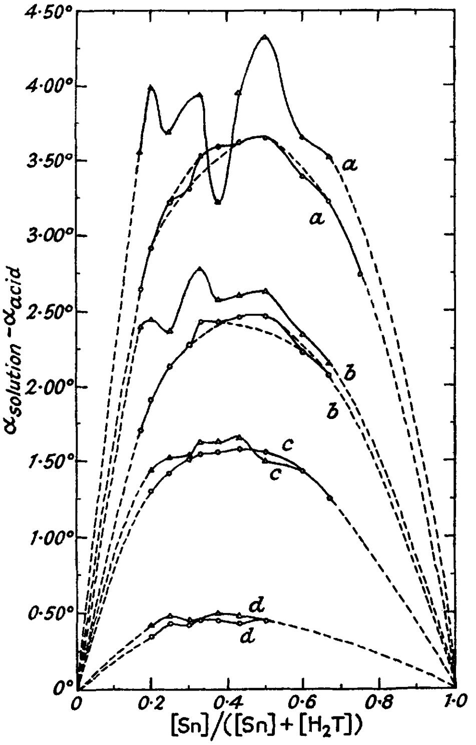
Absorption of carbon dioxide or attack on the vessel walls would have had the opposite effect; the phenomenon may have been due to slow desorption of hydroxyl ions during aggregation of micellar particles. Thus deposition of solid occurred above pH ~6, it being immediate above pH ~8.

(b) *Polarimetric measurements.* Measurements of $(\alpha_{\text{complex solution}} - \alpha_{\text{acid}})$ in the dilute series gave no definite maximum attributable to one complex when plotted against the solution composition, [Sn]/([Sn] + [tartaric acid]) (tartaric acid is henceforth referred to as H_2T). Such indefinite characteristics may be ascribed to the presence of more than one complex in solution. Vosburgh and Cooper (*J. Amer. Chem. Soc.*, 1941, **63**, 437) have shown, however, that when the property measured is sufficiently sensitive to change in complex concentration, then if the various species are easily interconvertible, identifiable maxima occur, displaced only slightly, if at all, from the true composition of the complexes to which they correspond. This was realised in more concentrated solutions, where separation is effected (Fig. 1). Two maxima are evident, at tin : tartrate ratios of 1 : 1 and 1 : 2, displaced and flattened somewhat from the effect of one maximum on the other. The broken lines represent extrapolations illustrating the situation where one species predominates. As the hydrochloric acid molarity increases, the extent of complex formation decreases (competitive action), and the 1 : 2 complex apparently becomes more predominant. These experimental results were fully reproducible.

In this series, solid hexachlorostannate was used (hydrochloric acid being added to reach the formal acidity), and considerable liberation of acid takes place on dissolution in the complexing acid. Since the optical rotatory power of free (+)-tartaric acid is affected by strong acids, the value of ($\alpha_{\text{complex solution}} - \alpha_{\text{acid}}$) is affected. By titration to the methyl-orange change with ammonia, this liberated acid was roughly estimated, and the corrections applied for in Fig. 1. It should be noted, however, that the positions of the maxima were the same on the " uncorrected " curve, where acid liberation was not allowed for.

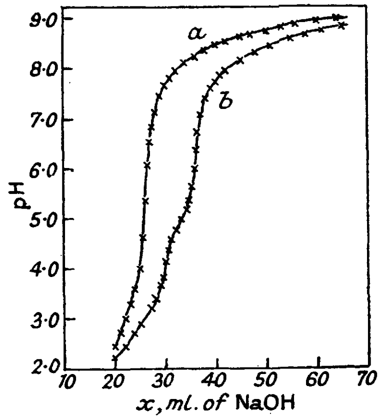
Effects of ageing. Ageing invariably caused an increase in the optical activity of the complex solutions (Fig. 1), it being most significant at the maxima. In the dilute ammoniacal series, many of the solutions became turbid quite rapidly after the first measurement, and after 1 day had deposited (presumably) basic tin tartrate. Solutions of higher tartrate content did not show such rapid changes, but deposition had occurred after 3 months. A new maximum is observable, corresponding to a 1[tin] : 4[tartrate] complex, presumably not present in sufficient amounts to affect the curve given by measurements on the fresh solutions.

FIG. 1. *Optical activity variation curves for tin and tartaric acid.*



O = Fresh solutions. Δ = Aged solutions.
(*a*) Sn–H_2T. (*b*) Sn–H_2T, 0·5N in HCl.
(*c*) Sn–H_2T, 0·9N in HCl. (*d*) Sn–H_2T, 1·8N in HCl.

FIG. 2. pH *Titration curves of germanium.*



x Ml. of 0·082N-NaOH against 1×10^{-4} mole of Ge (in 10 ml.) +
(*a*) $(90 - x)$ ml. of H_2O.
(*b*) 8·0 ml. of 0·05M-H_2T + $(82 - x)$ ml. of H_2O.

(c) *Polarographic measurements.* No reduction wave is produced in alkaline, neutral, or acid stannic–tartrate solutions; apparently the rate of reduction of the complex ions is too slow for any appreciable reduction to occur during the short life of a mercury drop. Lingane (*J. Amer. Chem. Soc.*, 1945, **67**, 919) has shown that stannic tin produces a well-defined doublet wave in solutions approximately 4M with respect to chloride ions (M in hydrochloric acid), corresponding to $SnCl_6^{--} \longrightarrow SnCl_4^{--}$ (−0·25 v against S.C.E.), followed by $SnCl_4^{--} \longrightarrow$ metal (−0·52 v against S.C.E.). The combined diffusion currents are proportional to the tin concentration. Addition of tartaric acid reduces the tin concentration, and hence the total diffusion current, by complex formation. For the equilibrium $SnCl_6^{--} + m\text{HT}^- \rightleftharpoons SnCl_{6-m}(\text{HT})_m^{--} + m\text{Cl}^-$, HT^- being assumed to be the complex-forming species, the classical equilibrium constant is given by

$K = [SnCl_{6-m}(HT)_m^{--}][Cl^-]^m/[SnCl_6^{--}][HT^-]^m$. Experimentally, $[SnCl_{6-m}(HT)_m^{--}]/[SnCl_6^{--}]$ is determinable by measuring the diffusion current before and after addition of tartaric acid, while $[Cl^-]$ and $[HT^-]$ are known, and kept constant in a given run. By varying $[HT^-]$, two equations are obtained from which the two unknowns, K and m, may be evaluated, *on the assumption that* m (an average combining ratio) *does not vary on change of* $[HT^-]$.

The values of K and m, $1{\cdot}2 \times 10^3$ and 1·03 (A), respectively, obtained from solutions 1·5M in hydrochloric acid, are in reasonable agreement with those obtained in 0·5M-hydrochloric acid, *viz.*, $2{\cdot}1 \times 10^3$ and 1·13 (B) (Table 1). (The mercury drop weight and time were kept constant throughout.) Greater agreement cannot be expected in view of neglect of activity corrections and experimental limitations on the accuracy of diffusion current measurment (changes in $D^{\frac{1}{2}}$, the diffusion coefficient term of Ilkovic's diffusion current expression, are probably not significant). The values (A) are more reliable, since they were obtained under conditions more suitable for reversible-wave formation. It thus appears that the predominant complex formed in these stannic–tartrate solutions is the 1 : 1 species.

TABLE 1. *Diffusion currents of tin in chloride–tartrate medium*

Concentration of tin = $5{\cdot}0 \times 10^{-3}$ mole/l.; 0·005% of gelatin present.

(A) HCl, M	NH_4Cl, M	H_2T, M	i *	(B) HCl, M	NH_4Cl, M	H_2T, M	i
1·5	3·0	—	43·25	0·5	2·5	—	43·25
1·5	3·0	0·2	41·63	0·5	2·5	0·2	40·50
1·5	3·0	0·5	39·00	0·5	2·5	0·5	36·00

K (see above) = $1{\cdot}2 \times 10^3$; m = 1·03. $K = 2{\cdot}1 \times 10^3$; m = 1·13.

* i = Microampères at constant drop weight and time.

(II) *Germanium.*—(a) pH *Measurements.* Reproducible curves were obtained on titrating germanium–tartrate solutions against sodium hydroxide; the pH values did not vary within 24 hours (cf. tin series). Fig. 2 shows the existence of two end-points in the complex solution, the first representing the neutralisation of the hydrochloric acid present, and the second that of the tartaric acid. The liberation of hydrochloric acid on complex formation is indicated by comparison with the curve for non-complexed germanium. The value thus obtained by difference may be only approximate, since it assumes similar hydrolysis and aggregation characteristics in both types of solution, and experimentally, buffering made end-points difficult to identify. Approximately $3{\cdot}2 \times 10^{-4}$ mole of hydrogen ion was liberated by $1{\cdot}0 \times 10^{-4}$ mole of germanium on complex formation (Table 2). This is perhaps best explained by reactions such as

$$\left\{\begin{array}{l} GeCl_6^{--} + H_2T \longrightarrow GeCl_4\,(T)^{--} + 2HCl \\ GeCl_6^{--} + 2H_2T \longrightarrow GeCl_2\,(T)_2^{--} + 4HCl \end{array}\right.$$

TABLE 2. pH *Titrations of germanium solutions.*

$1{\cdot}0 \times 10^{-3}$ mole/l. of Ge + $4{\cdot}0 \times 10^{-3}$ mole/l. of complex-forming acid against 0·082N-NaOH.
HCl titre of blank Ge solution = 26·0 ml. of NaOH. Total solution vol. = 100 ml.

(A) Tartaric acid.
HCl titre = 30·0 ml. of NaOH.
H_2T titre = 6·0 ml. of NaOH ≡ $2{\cdot}45 \times 10^{-4}$ mole of $[H_2T]$.
HCl liberated ≡ 4·0 ml. of NaOH ≡ $3{\cdot}26 \times 10^{-4}$ mole of $[H^+]$

Since $4{\cdot}0 \times 10^{-4}$ mole of $[H_2T]$ had been added $(4{\cdot}0 - 2{\cdot}45) \times 10^{-4}$ mole was removed by complex formation = $1{\cdot}55 \times 10^{-4}$ mole of $H_2T \equiv 3{\cdot}12 \times 10^{-4}$ mole of $[H^+]$.

$$1{\cdot}0 \times 10^{-4}\ Ge + 4{\cdot}0 \times 10^{-4}\ H_2T \longrightarrow 3{\cdot}26 \times 10^{-4}\ HCl + 2{\cdot}45 \times 10^{-4}\ H_2T \text{ (all in moles).}$$

(B) Malic acid } Same end-point data. Titration curves more buffered the weaker the acid
(C) Succinic acid } ($K_{H_2T} > K_{H_2M} > K_{H_2Succ.}$).

the participation of a $GeCl_6^{--}$ ion being assumed for simplicity of representation. [$GeCl_{6-x}(OH)_x^{--}$ would, for example, be a more general picture of the monomeric ion]. This then correlates with the complex-forming ratios of 1 : 1 and 1 : 2 found for tin. It is noteworthy that malic and succinic acids gave essentially the same results, suggesting similar behaviour by these acids on complex-formation with germanium. The evidence is by no means independently conclusive, however.

(b) *Polarimetric measurements.* Figs. 3 and 4 show variation curves for germanium–tartrate systems in hydrochloric acid and ammoniacal media (all results were completely reproducible). In all the acid series a well-defined maximum manifests itself at the composition 1[Ge] : 1[H_2T], acidity change altering the complex concentration (indicated by activity values) negligibly.

Curvature, becoming more pronounced as the acidity decreases, suggests the existence of more than one complex species.

The ammoniacal series show that the 1 : 2 complex may be this other species. The apparent lævorotation at high germanium : tartrate ratios may be indicative of yet another complex, but it was not possible to extend the curve to a turning point, owing to precipitations occurring before measurement could be made. The simplest species would be the 2 : 1 complex.

Effects of ageing. As with tin, ageing caused an increase in rotation for the acid series, without change in the maximum position. After 3 months, the activity remained constant. In the ammoniacal solutions, precipitation occurred quite rapidly.

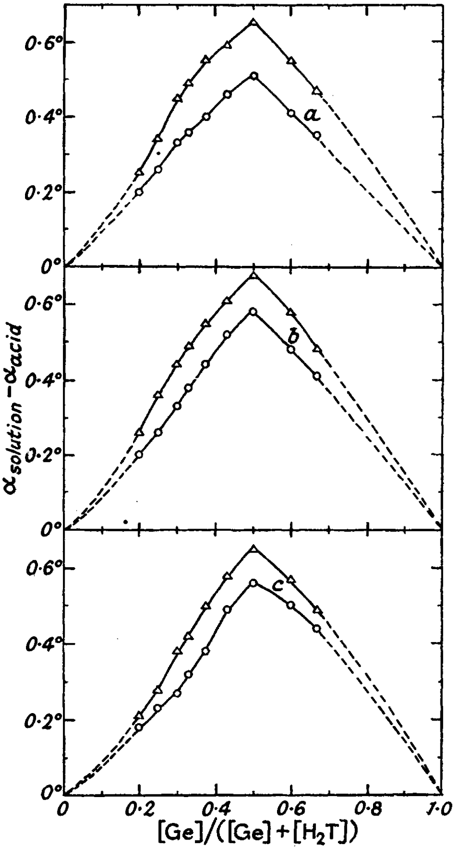
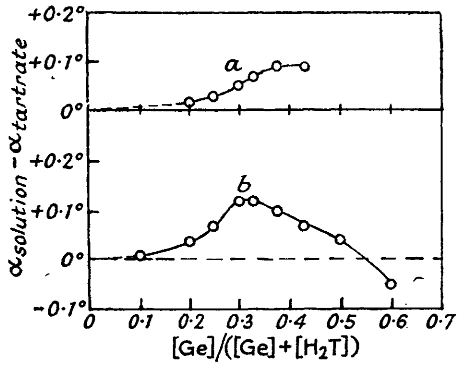


FIG. 3. *Optical activity variation curves for germanium and tartaric acid.*

○ = Fresh solutions. Δ = Aged solutions.
(*a*) Ge–H_2T, 2N in HCl. (*b*) Ge–H_2T, N in HCl.
(*c*) Ge–H_2T, 0·1N in HCl.

FIG. 4. *Optical activity variation curves for germanium and tartaric acid.*



(*a*) Ge–H_2T, 0·5N in NH_4OH.
(*b*) Ge–H_2T, 0·1N in NH_4OH.

(c) *Polarographic measurements.* No wave attributable to reduction of a complex was observed in germanium–tartrate solutions under acid or alkaline conditions.

(III) *Titanium.*—(a) pH *Measurements.* A preliminary "static" titration of a solution containing titanium and tartaric acid in the ratio 3 : 4 gave non-reproducible results, although

TABLE 3. pH *Titrations of titanium solutions.*

$1{\cdot}0 \times 10^{-3}$ mole/l. of Ti + $4{\cdot}0 \times 10^{-3}$ mole/l. of complex-forming acid against 0·05N-NaOH.
HCl titre of blank Ti solution = 20·5 ml. of NaOH. Total solution vol. = 100 ml.

(A) Tartaric acid.
HCl titre = 26·5 ml. of NaOH.
H_2T titre = 11·5 ml. of NaOH $\equiv 2{\cdot}6 \times 10^{-4}$ mole of [H_2T].
HCl liberated = 6·0 ml. of NaOH $\equiv 3 \times 10^{-4}$ mole of [H^+].

Since $4{\cdot}0 \times 10^{-4}$ mole of [H_2T] had been added, $(4{\cdot}0 - 2{\cdot}6) \times 10^{-4}$ mole was removed by complex formation = $1{\cdot}4 \times 10^{-4}$ mole of $H_2T \equiv 2{\cdot}8 \times 10^{-4}$ mole of [H^+].

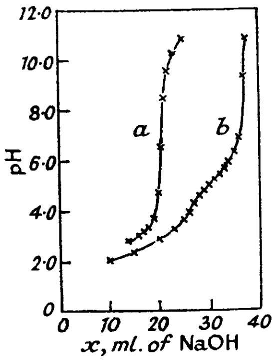
$$1{\cdot}0 \times 10^{-4}\ \text{Ti} + 4{\cdot}0 \times 10^{-4}\ H_2T \longrightarrow 3{\cdot}0 \times 10^{-4}\ \text{HCl} + 2{\cdot}6 \times 10^{-4}\ H_2T \text{ (all in moles).}$$

(B) Malic acid
(C) Succinic acid } Same end-point data. Titration curves more buffered the weaker the acid.

the pH did not vary greatly with time. However, at a higher tartaric acid concentration (ratio = 1[Ti] : 4[H_2T]), reasonable reproducibility was achieved, the curve giving end-point data (Table 3 and Fig. 5) similar to those for germanium; again, malic and succinic acids behaved similarly to tartaric acid. No observable variation in pH had occurred after a period of two months.

The similarity in behaviour of titanium and germanium suggests a similarity in the complex-forming processes. Bearing in mind the reservations mentioned in (II), it may be inferred that 1 : 1 and 1 : 2 complex formation occurs between titanium and tartaric, malic, or succinic acids.

FIG. 5. pH *Titration curves of titanium.*



x Ml. of 0·05N-NaOH against 1×10^{-4} mole of Ti (in 10 ml.) +

(*a*) (90 − *x*) ml. of H_2O.
(*b*) 20 ml. of 0·02M-H_2T + (70 − *x*) ml. of H_2O.

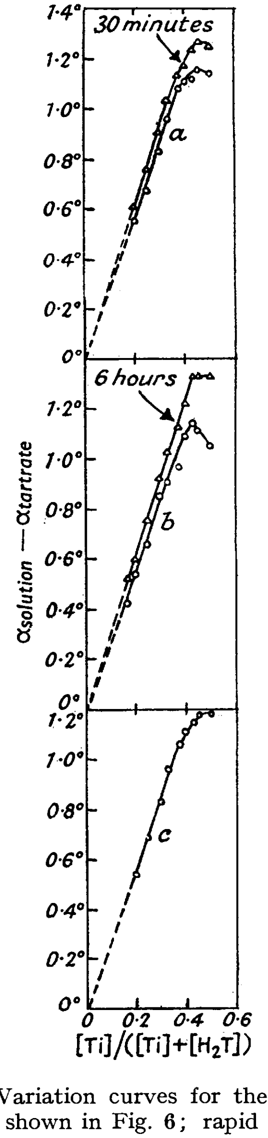
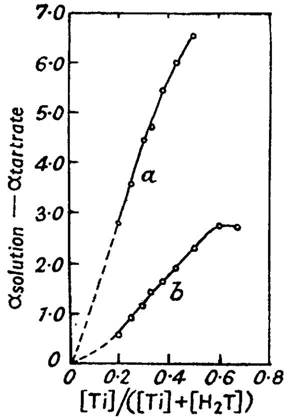


FIG. 6. *Optical activity variation curves for titanium and tartaric acid.*

○ = Measurements after 3 minutes.

(*a*) Ti-H_2T, N in NH_4OH.
(*b*) Ti-H_2T, 0·5N in NH_4OH.
(*c*) Ti-H_2T, 0·1N in NH_4OH.

FIG. 7. *Optical activity variation curves for titanium and tartaric acid.*



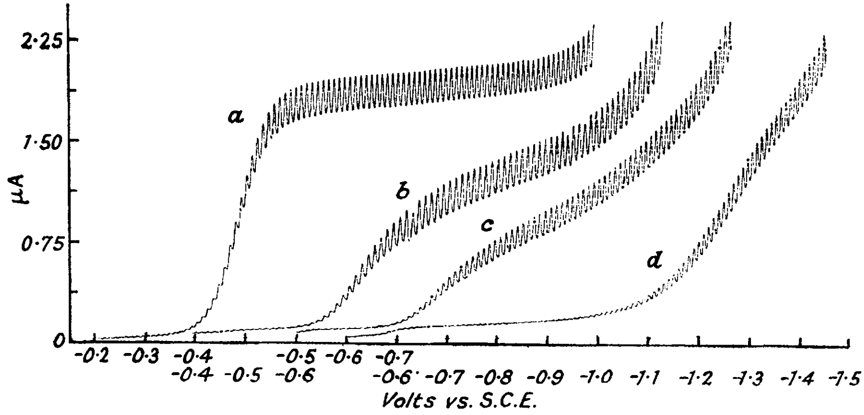
(*a*) Ti-H_2T, 0·5N in HCl.
(*b*) Ti-H_2T, N in HCl.

(b) *Polarimetric measurements.* Variation curves for the optical activity of ammoniacal dilute titanium–tartrate systems are shown in Fig. 6; rapid precipitation prevented measurements from being made at [Ti]/([Ti] + [H_2T]) ratios greater than 0·50. In acid medium, good reproducibility was not obtained, owing to low activity values and sensitivity to slight changes in acidity.

Precipitation also restricted measurements at the more concentrated level. Here, as in the dilute series, definite maxima are not evident (Fig. 7).

Effects of ageing. As in (I) and (II), ageing brought about a rise in the activity (Fig. 6). Basic solids were precipitated, the time before deposition decreasing as the [Ti] : [H_2T] ratio

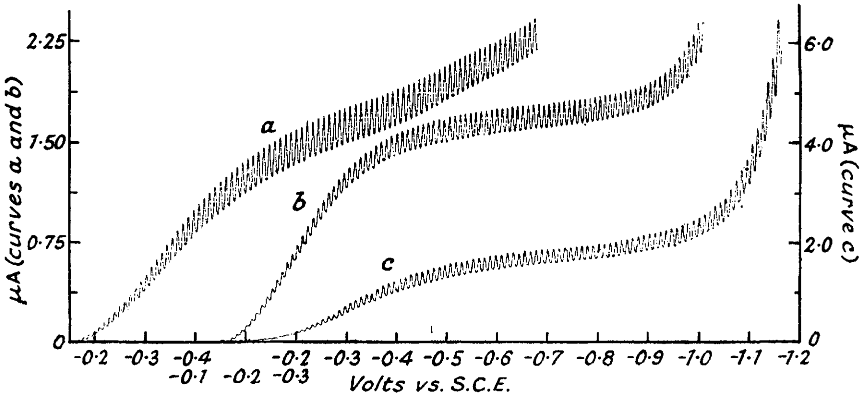
FIG. 8. *Effect of* pH *on reduction wave of titanium*(IV) *in tartaric acid solution.*



$1\cdot0 \times 10^{-4}$ mole of Ti/l.; 0·2M in H_2T.

(*a*) pH = 1·22; $E_{\frac{1}{2}} = -0\cdot48$ v.
(*b*) pH = 2·37; $E_{\frac{1}{2}}$ indeterminate.
(*c*) pH = 2·76; $E_{\frac{1}{2}}$ indeterminate.
(*d*) pH = 3·99; $E_{\frac{1}{2}}$ indeterminate.

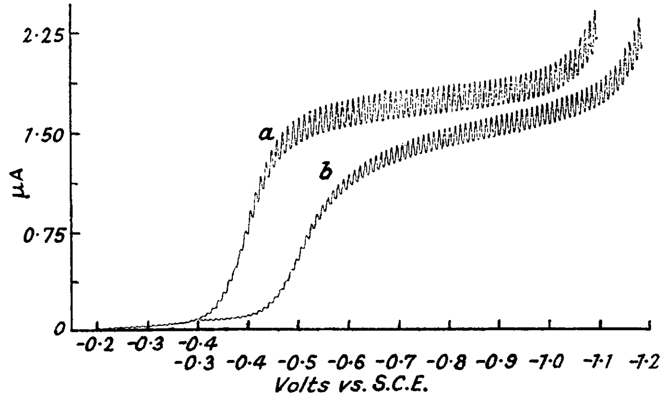
FIG. 9. *Effect of acid strength on reduction wave of titanium*(IV).



$1\cdot0 \times 10^{-3}$ mole/l.

(*a*) M in HCl, 0·2M in H_2T; $E_{\frac{1}{2}}$ indeterminate.
(*b*) M in HCl, 0·5M in H_2T; $E_{\frac{1}{2}} \sim -0\cdot31$ v.
(*c*) M in HCl, 3M in NH_4Cl; $E_{\frac{1}{2}}$ indeterminate.

FIG. 10. *Effect of tartaric acid concentration on reduction wave of titanium*(IV) *in tartaric acid.*



$1\cdot0 \times 10^{-3}$ mole/l.

(*a*) 0·5M in H_2T; $E_{\frac{1}{2}} = -0\cdot51$ v.
(*b*) M in H_2T; $E_{\frac{1}{2}} \sim -0\cdot52$ v.

increased. In the acid concentrated solutions, salting out occurred in all solutions, without prior activity increase.

Apparently the titanium–tartrate complexes exist in sluggish equilibrium with each other. The indications are that a 2 : 1 complex exists in acid concentrated solutions, together with others which may be the 1 : 1 and 1 : 2 species. The presence of these two would account for the maximum at 3 : 4 in the ammoniacal series. Condensed species (such as the 2 : 3 complex suggested by Caglioti) are highly probable, also.

(c) *Polarographic measurements.* Although it has frequently been demonstrated that titanium in an excess of tartaric acid solution gives a reversible reduction wave (Pecsok, *J. Amer. Chem. Soc.*, 1951, **73**, 1304; Strubl, *Coll. Czech. Chem. Comm.*, 1938, **10**, 475; Caglioti and Sartori, *loc. cit.*), the effect of varying the conditions has not been greatly studied. Various constraints were therefore applied :

(i) Effect of pH. The polarograms of $1{\cdot}0 \times 10^{-3}$M-titanium in 0·2M-tartaric acid at varying pH (controlled by addition of sodium hydroxide) are shown in Fig. 8. Increasing the pH is shown to destroy rapidly the reversible nature of the waves, and reduction occurs at more negative potentials. Above pH $\sim$4, no wave due to titanium is obtained. These are effects similar to those observed for titanium–oxalic acid solutions (Pecsok, *loc cit.*). Apparently as the pH increases, hydrolysis and aggregation render reduction more difficult.

(ii) Effect of acid strength. When the solution is made M in hydrochloric acid, the wave became less reversible than at pH $\sim$1, shifting to more positive potential values (Fig. 9, *a*). Increasing the tartaric acid content from 0·2 to 1·0M somewhat counteracts this effect (Fig. 9, *b*). It is probable that, as the hydrochloric acid content is increased relative to that of the tartaric acid, the competing effect of the strong acid dissociates the tartrate complex, and the wave assumes a shape approaching that given by titanium in chloride medium (Fig. 9, *c*).

(iii) Effect of tartaric acid concentration. In Fig. 10 it is demonstrated that increasing the tartaric acid concentration causes the wave to become less reversible, and the half-wave potential is shifted to more negative values (see also Fig. 8, *a*). The tendency to irreversibility is due either to large quantitites of tartaric acid decreasing the reduction rate at the dropping electrode (large quantities of neutral salts sometimes exhibit this effect : see Cambridge Instrument Co. polarograph manual) or to the formation of a second complex in appreciable quantities, both species being reduced at similar potentials.

DISCUSSION

The evidence here presented points very strongly to 1 : 1 and 1 : 2 complex formation of metal : tartrate for the three elements examined, and similar behaviour is inferred with malic or succinic acids as complex-forming agents. There is no doubt, however, that other complexes exist under different conditions, polynuclear species included.

The extreme difficulty of identifying each ionic species is clearly seen when it is remembered that, except in very strongly acid solutions, considerable hydrolysis takes place. Although a 1 : 1 or 1 : 2 complex may be identifiable, the number of hydroxyl groups in the ion varies. Unless the concentrations of each individual species are known, dissociation constants cannot be calculated; failure to appreciate this has vitiated some earlier work (cf. Caglioti, p. 990). The polarographic measurements show clearly the marked effect of pH change. It is also to be borne in mind that hydrolysis here precedes aggregation, which may be considerable, thereby further complicating the analysis.

The ageing phenomena noted are consistent with a slow aggregation process following rapid hydrolysis, by means of intermolecular condensation. This may be achieved in a variety of ways, the species growing in size to become micellar or colloidal, eventually to be precipitated if conditions permit the process to continue. Such tendencies would be favoured by low acidity (or alkaline conditions), high metal concentration relative to complex-forming agent concentration (or high concentration in general), and presence of salting-out electrolytes. These have all been demonstrated.

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