26. *Physico-chemical Studies of Complex Formation Involving Weak Acids. Part IV. Alkali Solutions of Lanthanum Tartrate.*

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THE dissolution of lanthanum tartrate in solutions of either alkalis or alkali tartrates is an excellent example of the property possessed by hydroxy-acids of holding certain metallic bases in solution even though the p_H values of such solutions may be very much higher than those at which the bases themselves normally become precipitable. Britton (J., 1926, 293) found that normal lanthanum tartrate, besides being soluble in alkalis and alkali tartrates, dissolves in a large excess of either tartaric acid or sodium bitartrate. The solubility in these last two cases is in all probability governed by solubility-product requirements, each of these reactants eventually establishing tartrate-ion concentrations which, owing to the small second ionisation constant of tartaric acid, are lower than that necessary to exceed the solubility product of lanthanum tartrate. Although little work was done on the cause of the solubility in sodium hydroxide solutions, definite indications were obtained that the lanthanum tartrate did not exist as such in these solutions, but as a basic tartrate. Conductivity and *E.M.F.* measurements have now been employed in a further study of the problem.

EXPERIMENTAL.

1. *Conductometric Titrations.*—Lanthanum tartrate dissolves in sodium tartrate solutions only when the latter is in considerable excess; but it dissolves readily in sodium hydroxide solution especially in presence of sodium tartrate. Two series of conductometric titrations were therefore performed at 25° with a view to investigate the mode of dissolution in these two types of solution.

FIG. 1.

Equivs. Sodium Tartrate (curves I and II).
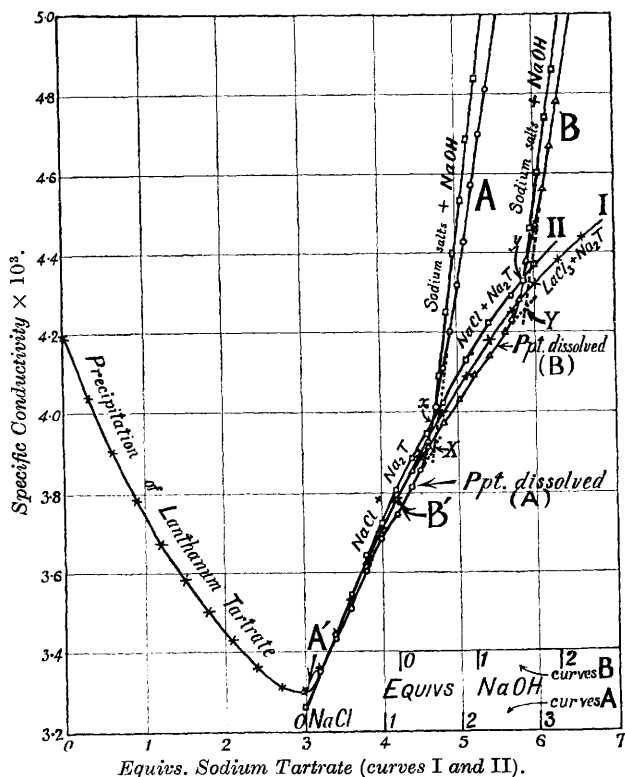
In the first place, the specific conductivities of solutions, obtained by adding $0.05M$-sodium tartrate solution to 75 c.c. of $0.01333M$-lanthanum chloride solution, were measured. These are recorded in columns A of Tables I and II for amounts of sodium tartrate in excess of 30 c.c. (the amount required for the precipitation of lanthanum tartrate) and 42 c.c., respectively. The variation in specific conductivity is also plotted in Fig. 1, in which the first section corresponds to the precipitation of lanthanum tartrate, and the second (curve I) to the addition of an increasing excess of

sodium tartrate. The specific conductivity of the mother-liquor on the addition of 3 equivs. of sodium tartrate, *i.e.*, $3Na_2T$ to $2La$, is seen to be slightly greater than would have been the case if the solution had contained only sodium chloride, the difference apparently being due to the slight solubility of the lanthanum tartrate. To ascertain whether any lanthanum tartrate was being dissolved during the progressive addition of sodium tartrate, a sodium chloride solution was prepared having the same volume and concentration as that of the mother-liquor when precipitation had become complete. To this solution $0.05M$-sodium tartrate solution was added. The variations in the specific conductivities thus set up are recorded in columns B of Tables I and II, and plotted (curve II) in Fig. 1. Curves I and II are not quite congruent, and reveal that the presence of the suspended lanthanum tartrate is responsible for a very small diminution in the conductivity of the sodium tartrate, this effect becoming greater with increasing excess of sodium tartrate.

The next conductometric titration was of a solution of sodium chloride and precipitated lanthanum tartrate with $0.1N$-sodium hydroxide. The solution was prepared by mixing 75 c.c. of $0.01333M$-lanthanum chloride with 30 c.c. of $0.05M$-sodium tartrate. The data obtained are recorded in Table I, column C, and are plotted on curve A in Fig. 1. The lanthanum tartrate dissolved when 1·4 equivs. of alkali had been added (14·0 c.c.). The change in specific conductivity prior to the dissolution of the lanthanum tartrate is seen to be almost the same as that previously obtained when the titrant was sodium tartrate, and it therefore appears that the sodium hydroxide must have been converted into sodium tartrate by reaction with the suspended lanthanum tartrate. Despite this attack, it was ascertained by parallel experiments that no lanthanum passed into solution until its tartrate had been rendered sufficiently basic for its dissolution to take place. Soon after the precipitate had dissolved, a break was observed in the titration curve, at x, after which additions of alkali caused a rapid increase in specific conductivity.

It was suspected that this sharp increase was due to the presence in the solution of free alkali which had ceased further to attack the dissolved basic tartrate. To prove this, the exact amount of alkali required to produce the basic tartrate was estimated by drawing tangents to the two sections of curve A and finding the point of intersection, X. This point corresponded to the addition of 16·5 c.c. of $0.1N$-sodium hydroxide, and therefore the composition of the soluble basic tartrate would then have been $La_2(OH)_{3.30}T_{1.35}$. A solution, of the same volume as that of the

TABLE I.

Conductometric titration of lanthanum tartrate.

A. 75 C.c. 0·01333M-LaCl₃+30 c.c. 0·05M-Na₂T with 0·05M-Na₂T.		B. 105 C.c. 0·02857M-NaCl with 0·05M-Na₂T.		C. 75 C.c. 0·01333M-LaCl₃+30 c.c. 0·05M-Na₂T with 0·1M-NaOH.		D. 105 C.c. 0·02857M-NaCl+16·5 c.c. 0·05M-Na₂T with 0·1M-NaOH.	
Na₂T, c.c.	$\kappa \times 10^3$.	Na₂T, c.c.	$\kappa \times 10^3$.	NaOH, c.c.	$\kappa \times 10^3$.	NaOH, c.c.	$\kappa \times 10^3$.
0	3·30	0	3·26	0	3·30		
2	3·36	2	3·35	2	3·35		
4	3·45	4	3·44	4	3·43		
6	3·53	6	3·54	6	3·52		
8	3·62	8	3·64	8	3·60		
10	3·70	10	3·72	10	3·68		
12	3·78	12	3·80	12	3·74		
		14	3·88	14	3·81		
15	3·89	15	3·91	15	3·85		
		16	3·94	16	3·92		
				17	4·01	0	3·98
18	3·99	18	4·02	18	4·11	0·5	4·04
				19	4·20	1·5	4·18
20	4·06	20	4·09	20	4·32	2·5	4·32
21	4·09	21	4·13	21	4·44	3·5	4·46
				22	4·56	4·5	4·60
				23	4·69	5·5	4·74
24	4·18	24	4·22	24	4·81	6·5	4·87
27	4·25	27	4·29	27	5·19		
30	4·32	30	4·37	30	5·58		

liquid at this stage of the titration, containing no lanthanum, but the same amount of sodium chloride and sodium tartrate—considered to have been formed by the interaction of the added alkali—was treated with alkali and the variations in conductivity noted. The titration curve commences from the point x, and whilst its slope is approximately that of the corresponding section of the lanthanum tartrate curve, it shows that the specific conductivities of the alkaline lanthanum tartrate solutions are somewhat lower, the difference increasing with the amount of alkali added. It would therefore appear that the basic lanthanum tartrate in solution was still being decomposed by the alkali but only to a comparatively slight extent. The data for this titration are given in Table I, column D.

In the second series of conductometric titrations, 1·2 equivs. of sodium tartrate were added in excess, and the reaction with alkali studied. The details are given in Table II, column C, and the titration curve is B in Fig. 1. The curve begins at B' on curve I and once again the alkali curve falls a little below the sodium tartrate curve, I. The precipitate dissolved when 1·3 equivs. of alkali had been added, *i.e.*, some time before the rapid increase in specific conductivity occurred. The composition of the basic com-

plex was ascertained from the position of the point Y, viz., $La_2(OH)_{3\cdot30}T_{1\cdot35}$, and a similar titration of alkali salts with sodium hydroxide (column D, Table II), when plotted (Fig. 1), again revealed that the soluble basic tartrate gradually removed alkali from the solution in being rendered more basic.

TABLE II.

Conductometric titration of lanthanum tartrate in presence of a small excess of sodium tartrate.

A. 75 C.c. 0·01333M-LaCl$_3$+42 c.c. 0·05M-Na$_2$T with 0·05M-Na$_2$T.		B. 105 C.c. 0·02857M-NaCl+12 c.c. 0·05M-Na$_2$T.		C. 75 C.c. 0·01333M-LaCl$_3$+42 c.c. 0·05M-Na$_2$T with 0·1M-NaOH.		D. 105 C.c. 0·02857M-NaCl+28·5 c.c. 0·05M-Na$_2$T with 0·1M-NaOH.	
Na$_2$T, c.c.	$\kappa \times 10^3$.	Na$_2$T, c.c.	$\kappa \times 10^3$.	NaOH, c.c.	$\kappa \times 10^3$.	NaOH, c.c.	$\kappa \times 10^3$.
0	3·78	0	3·80	0	3·78		
				2	3·85		
4	3·93	4	3·94	4	3·91		
				6	3·97		
8	4·06	8	4·09	8	4·03		
				10	4·09		
12	4·18	12	4·22	12	4·14		
				14	4·20		
				15	4·23		
16	4·28	16	4·32	16	4·28		
						0	0·433
				17	4·38	0·5	0·439
18	4·32	18	4·37	18	4·47	1·5	0·452
				19	4·56	2·5	0·464
				20	4·67	3·5	0·477
				21	4·78	4·5	0·490
				23	5·01	6·5	0·516

2. *Potentiometric Titrations with the Hydrogen Electrode.*—A series of hydrogen-electrode titrations was carried out to study the reaction between sodium hydroxide and lanthanum tartrate suspended in water containing (i) sodium chloride and (ii) sodium chloride and an excess of sodium tartrate. 75 C.c. of 0·01333M-lanthanum chloride were mixed with 30 c.c. of (i) 0·05M-, (ii) 0·25M-, and (iii) 1·0M-sodium tartrate and titrated with 0·1N-sodium hydroxide; the excess sodium tartrate in these titrations was thus 0, 12, and 57 mols. respectively to each mol. of lanthanum tartrate. The p_H curves are plotted on the left of Fig. 2. All three curves are similar, and indicate that sharp changes in p_H began immediately after 2 mols. of alkali had been added to 1 mol. of lanthanum tartrate. The solutions had become appreciably alkaline some time before 4 mols. (instead of the 6 mols. required to convert the lanthanum tartrate completely into hydroxide) had been added. The influence of sodium tartrate in causing the basic lanthanum tartrate to dissolve on the addition of a smaller

quantity of alkali was again observed, for dissolution occurred at 2·8, 2·2, and 0·8 mols. of alkali respectively. The curves reveal, since the inflexions are almost identical, that the composition of the basic lanthanum tartrate in each of the three solutions must have been similar. The smaller inflexion in the last two titrations


Fig. 2.

Mols. NaOH.
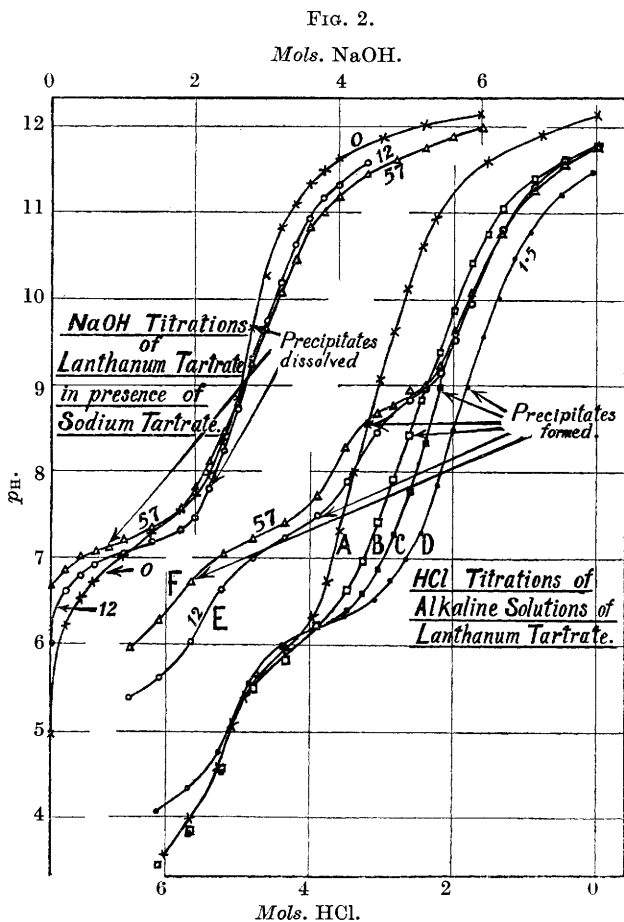
suggests that the basic complexes in the presence of sodium tartrate are a little more readily attacked by alkali.

By comparing the conductometric curves in Fig. 1 with the hydrogen-electrode curve for lanthanum tartrate and sodium hydroxide, it is seen that the actual breaks in the former occur at 3·30 mols. of alkali, corresponding to a point in the latter at which

H 2

the concentration of free alkali just begins to be sufficient to be reflected in the conductivity of the solution.

The compositions of the basic lanthanum tartrate complexes present in the solutions have been calculated and are given in Table III. For this purpose, it was assumed that the basic tartrates present in the solutions were formed as the result of the reaction $La_2(C_4H_4O_6)_3 + xNaOH \longrightarrow$

$$La_2(OH)_x(C_4H_4O_6)_{3-\frac{1}{2}x} + \tfrac{1}{2}xNa_2C_4H_4O_6.$$
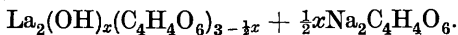
Such a view is justifiable, for the conductometric titrations show that it is extremely probable that in the initial part of the reaction the sodium hydroxide is converted quantitatively into sodium tartrate. Where the solution has acquired an alkaline reaction, it is possible from the p_H and the appropriate value of K_w, to calculate the hydroxyl-ion concentration, which may be assumed to be that of unattacked sodium hydroxide. From this is found the amount of alkali which has reacted with the lanthanum tartrate, and the composition of the basic tartrate is then given by the above equation.

TABLE III.

Direct Titration.

Composition of soluble basic lanthanum tartrate, $La_2(OH)_x(C_4H_4O_6)_{3-\frac{1}{2}x}$.

Values of x.

Alkali added, Mols. NaOH	Mols. of sodium tartrate in excess =		
Mols. La_2T_3	0.	12.	57.
2·2		2·2 Diss.	
2·8	2·80 Diss.		
3·0	2·98	3·00	3·00
4·0	3·50	3·74	3·80
5·0	3·90	—	4·28
6·0	4·26	—	4·48

It will be seen from Table III that the presence of a considerable excess of sodium tartrate in the mother-liquor results in the lanthanum tartrate dissolving before it has become highly basic. In every case the addition of alkali effected a further partial decomposition of the basic tartrate that had previously passed into solution. The figures in Table III do not give any indication of the formation of a basic lanthanum tartrate of definite composition. Calculations of its composition in solutions to which a large excess of alkali had been added showed that basic tartrates existed therein, but the errors inherent in the computations were such as to prevent any precise significance being attached to the results.

The next titrations were performed to ascertain whether the composition of the dissolved basic tartrate was in any way dependent on the mode of treatment of the alkaline solutions. Three back-

titrations with hydrochloric acid were therefore carried out of complex lanthanum tartrate solutions to which had been added the amount of alkali theoretically necessary to form lanthanum hydroxide. The first was done immediately after mixing the reactants, the second after the complex solution had assumed a condition of equilibrium during prolonged standing, and the third after short boiling followed by cooling. Their respective titration curves are A, B, and C in Fig. 2, and the compositions of the soluble basic tartrates are recorded in Table IV in the respective columns

TABLE IV.

Back-titration of mixtures of 75 c.c. of 0·01333M-lanthanum chloride, 30 c.c. of 0·05M-sodium tartrate, and 30 c.c. of 0·1N-sodium hydroxide, with 0·1N-hydrochloric acid.

Compositions of soluble basic lanthanum tartrate, $La_2(OH)_x(C_4H_4O_6)_{3-\frac{1}{2}x}$.

Values of x.

HCl, mols.	A.	B.	C.
0	4·26	5·02	5·00
0·5	4·24	4·84	4·76
1·0	4·14	4·64	4·56
1·5	3·94	4·40	4·38
2·0	3·78	3·98	4·00
2·18			3·82 ppt.
2·5	3·46	3·50	
2·6		3·40 ppt.	
3·0	2·98		
3·2	2·80 ppt.		

A, B, and C. In the first column the amount of hydrochloric added is given in terms of mols. of HCl per mol. of $La_2(C_4H_4O_6)_3$. Ageing and boiling are seen to have the effect of decomposing the basic tartrate a little beyond that occurring on the simple mixing of the reactants. The boiled solution began to precipitate when the p_H had fallen to 8·97 and 2·18 mols. of hydrochloric acid had been added; the solution that had stood required more acid, *viz.*, 2·6 mols. and a lower p_H 8·43; and, in the immediate titration, precipitation was delayed until 3·2 mols. of acid had been added and p_H 8·55 attained. The final inflexion in the curves A, B, and C occurs before the addition of 6 mols. of acid, showing that the precipitated lanthanum tartrate was still basic.

Table IV indicates that the soluble basic tartrate became less basic as the hydrochloric acid was added. It is probable therefore that a fresh equilibrium was tending to be set up between the solution and a salt of increasing tartrate content. The added acid appeared first to react with the basic complex, but the final equilibrium was only set up, after a considerable time, by a further reaction—between the complex and sodium tartrate—and to

account for the slowness of this it is suggested that the basic tartrate is pseudo-colloidal.

To ascertain whether the presence of an excess of alkali tartrate in complex lanthanum tartrate solution conferred increased stability on the basic tartrate, two further titrations were carried out, the solutions containing sodium tartrate and lanthanum tartrate in the molar ratios of 12 : 1 and 57 : 1. The results (see curves E and F, Fig. 2) are given in cols. 3 and 4 of Table V; col. 2 is inserted for comparison, as it refers to the titration of the mixture of lanthanum tartrate and caustic soda alone shown in curve B, Fig. 2. Each of the mixtures used in these titrations had stood for 14 days before titration. Table V shows that the compositions of the complexes in each of the titrations were almost identical during the addition of the first 2 mols. of hydrochloric acid. The appearance of precipitates from the solutions was considerably delayed : the first solution showed a precipitate at p_H 7·49 with 3·92 mols. of acid, and the second at p_H 6·72 with 5·66 mols.

TABLE V.

Back-titrations of mixtures of 75 c.c. of 0·01333M-lanthanum chloride, 30 c.c. of yM-sodium tartrate, and 30 c.c. of 0·1M-sodium hydroxide after standing, with 0·1N-hydrochloric acid.

Composition of soluble basic lanthanum tartrate, $La_2(OH)_x(C_4H_4O_6)_{3-\frac{1}{2}x}$.

Values of x.

	yM-Sodium tartrate.		
HCl, mols.	0·05M.	0·25M.	1·00M.
0	5·02	4·98	4·98
0·5	4·84	4·86	4·88
1·0	4·64	4·74	4·76
1·5	4·40	4·46	4·46
2·0	3·98	4·00	4·00
2·5	3·50	3·50	3·50
2·6	3·40 ppt.	—	—
3·0	—	3·00	3·00
3·92	—	2·08 ppt.	—
5·66	—	—	0·34 ppt.

It is significant that precipitation occurred from solutions containing only a little sodium tartrate within the range p_H 8·4—9·0, for Britton (J., 1925, **127**, 2142) has shown that under normal conditions this is the range in which lanthanum hydroxide is precipitated. In the present circumstances the small amount of dissolved sodium tartrate appears to be responsible for the maintenance of the lanthanum in solution above p_H 9. In the titrations of the solutions in which much sodium tartrate was present, precipitates did not separate until well below p_H 8. The " humps " in the titration curves, E and F, between p_H 8 and 9, however,

reveal that important changes were taking place in the solutions. The hydrochloric acid must have reacted with the basic tartrate to form a less basic complex, which, in the previous titrations, then began to precipitate. Precipitation did not occur in these titrations owing to the power possessed by the alkali tartrate of retaining the basic lanthanum tartrate in solution.

To see whether the addition of an excess of alkali to complex lanthanum tartrate solutions brought about an increased decomposition of the basic tartrate, a series of back-titrations with $0.1N$-hydrochloric acid was carried out (Table VI). The first four titrations refer to alkaline solutions in which the molar ratio of lanthanum tartrate to sodium tartrate was $1 : 1.18$. Of these, the first two were carried out directly after mixing in the cold, whereas the others were performed on mixtures that had previously been boiled. The data given in the last column, headed D, refer to curve D in Fig. 2, and correspond to a titration of a boiled mixture of 75 c.c. of $0.01333M$-lanthanum chloride, 45 c.c. of $0.05M$-sodium tartrate, and 45 c.c. of $0.1N$-sodium hydroxide; *i.e.*, $La_2T_3 : Na_2T = 1 : 1.5$.

TABLE VI.

Back-titrations of mixtures of 100 c.c. of $0.00957M$-*lanthanum chloride, 40 c.c. of* $0.05M$-*sodium tartrate, and y c.c. of* $0.0976N$-*sodium hydroxide, with* $0.1N$-*hydrochloric acid.*

Composition of soluble basic lanthanum tartrate, $La_2(OH)_x(C_4H_4O_6)_{3-\frac{1}{2}x}$.

Values of x.

$y =$ HCl, mols.	30	50	50 boiled	70 boiled	D boiled
0	4·62	4·78	5·20	5·21	5·30
1·0	4·32	4·42	4·80	4·84	4·90
1·78	—	—	—	—	4·22 ppt.
2·00	3·86	3·92	4·00	4·00	
2·08	—	—	—	3·92 ppt.	
2·12	—	—	3·84 ppt.		
2·50	3·48	3·48			
3·00	3·00	3·00 ppt.			
3·22	2·78 ppt.				

The numbers of mols. of hydrochloric acid given in the first column are those in excess of the amount equivalent to the sodium hydroxide added beyond that theoretically required to decompose the lanthanum tartrate. The data given in Table VI may thus be compared with those in the foregoing tables. The precipitates separated from the first two solutions at p_H 8·36 and 8·44 with 3·22 and 3·00 mols. of acid respectively. The solutions that had initially been boiled required rather less acid for precipitation, and the corresponding p_H's were higher, *viz.*, 8·81, 8·74, and 8·99 respectively. Table VI shows that the addition of an excess of

alkali causes the basic tartrate to be slightly more hydrolysed, so much so that in one titration the basic tartrate acquired a composition corresponding to $La_2(OH)_{5\cdot30}T_{0\cdot35}$.

Discussion.

The conductivity curves in Fig. 1 show that the dissolution of lanthanum tartrate in sodium hydroxide is accompanied by the formation of sodium tartrate. Whether this sodium tartrate is actually the cause of the lanthanum tartrate dissolving is not certain, although the experiments described above show that a greater concentration of free sodium tartrate causes dissolution on the addition of a smaller amount of alkali. Despite this, the curves in Fig. 1 reveal that the basic tartrates in the solutions on the attainment of alkalinity are very similar. Furthermore, there appears to be no definite stoicheiometrical relationship between the basic lanthanum tartrate and sodium tartrate in the complex solution; in fact the composition of the former depends on the treatment which has been accorded to the solutions.

Dissolution of the lanthanum tartrate does not occur until the added alkali has rendered it sufficiently basic. The process of dissolution has been studied over a period of several months. Suspensions of lanthanum tartrate in various concentrations of alkali were kept, and it was found that as the ratio of sodium hydroxide was increased, the precipitates did not dissolve but became more and more bulky and did not settle out even when left undisturbed for several months. When the amount of alkali was just insufficient to give a clear solution, the basic lanthanum tartrate assumed a translucent gelatinous form which dispersed itself throughout the entire volume of the mother-liquor. The mixture corresponding to the point at which dissolution appeared to be almost complete in the course of the above titrations, i.e., on the addition of 1·2 mols. of sodium hydroxide to 1 mol. of lanthanum, on standing, set to an almost transparent gel, whilst with increasing proportions of alkali, the liquids formed after standing became less viscous until 1·4 mols. of sodium hydroxide had been added, whereupon a clear solution was obtained. It thus appears that, besides the passing of some sodium tartrate into the solution, there is a gradual change in the colloidal form of the precipitate involving a diminution in the size of the dispersed particles. Since the difference between colloidal and true solutions is one of particle-size, it seems reasonable to imagine that when the precipitate actually ·disappeared, the dispersed particles were still undergoing diminution of size and that they finally acquired the dimensions necessary to give an optically clear solution. We are thus confronted with an

nstance o a solution in which the solute appears to have no precise chemical individuality, but resembles rather a dispersed colloid. Yet the solution gives no sign of heterogeneity such as is given by solutions that are definitely known to be colloidal. It would appear from these experiments that the sodium tartrate was in some way responsible for the peptisation of the basic lanthanum tartrate, though this process is facilitated by an increased concentration of hydroxyl-ions.

The effect of the hydroxyl-ion concentration, however, may be included in the condition of rendering the lanthanum tartrate sufficiently basic for dissolution to become possible. Sodium tartrate alone, if added in sufficient excess, dissolves lanthanum tartrate. It is likely that the large concentration of sodium tartrate first converts the lanthanum tartrate into a basic tartrate before effecting its dissolution. It is hoped to carry out some cataphoretic experiments on the solutions.

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