326. *Physicochemical Studies of Complex Formation involving Weak Acids. Part XVII. The System Sodium Oxalate–Thorium Oxalate–Water at 25°.*
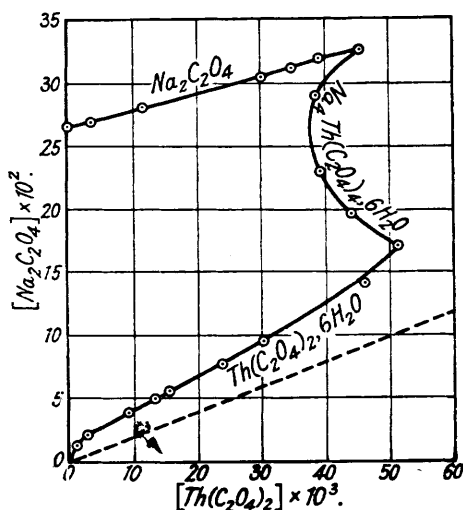
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The fact that thorium oxalate is soluble in solutions of ammonium oxalate was first observed by Bahr (*Annalen*, 1864, **132**, 231) and later used by Bunsen (*Pogg. Ann.*, 1875, **155**, 375) to separate thorium from the rare earths. Brauner (J., 1898, **73**, 951) attributed this increased solubility to the formation in solution of a definite ammonium thoroxalate, and isolated in crystalline form $(NH_4)_4Th(C_2O_4)_4,4$ and $7H_2O$. Cleve (*Bull. Soc. chim.*, 1874, **21**, 116) and Rosenheim, Samter, and Davidsohn (*Z. anorg. Chem.*, 1903, **35**, 424) isolated $K_4Th(C_2O_4)_4,4H_2O$ and $Na_4Th(C_2O_4)_4,6H_2O$ respectively.

We have carried out a phase-rule study of the system named in the title, and find that the sodium salt is only stable in the presence of excess of oxalate.

EXPERIMENTAL.

Thorium oxalate, obtained by precipitating thorium chloride solutions with oxalic acid, was washed and air-dried [Found : ThO_2, 51·20. Calc. for $Th(C_2O_4)_2,6H_2O$: ThO_2, 51·16%]. The sodium oxalate was of A.R. quality. Suitable mixtures of solutions of each oxalate were allowed to come to equilibrium (about 3 weeks) in a thermostat at $25° \pm 0·1°$. The oxalate contents of the liquid phases were determined by means of potassium permanganate, and the thorium as oxalate, precipitation being effected with oxalic acid from solutions 1—2N with respect to hydrochloric acid. To ascertain the composition of the solid phases, it was more convenient to filter them off by suction, remove adhering liquid as far as possible by pressure between filter-papers, and dry the solid in the air. The results obtained are given in the table and plotted in the figure, on which are indicated the solid phases with which the various liquid phases enter into equilibrium.

Brauner found that the ammonium complex salt is decomposed by water. The broken line in the figure represents aqueous solutions containing sodium oxalate and thorium oxalate in the molecular ratio 2 : 1, *i.e.*, the proportion in which the two oxalates occur in the complex salt corresponding with the central section of the isotherm. As the broken line does not intersect this section, it follows that $Na_4Th(C_2O_4)_4,6H_2O$ is also decomposed by water.

As shown by Britton (J., 1925, **127**, 2110), thorium hydroxide is normally precipitated at p_H 3·5. The p_H of the complex alkali oxalate solutions is in the vicinity of 7, showing that,

Liquid phase, g.-mols./l.		Solid phase, %.			Com-
$Na_2C_2O_4$.	$Th(C_3O_4)_2$.	Na.	C_2O_4.	Th.	pound.*
0·01002	0·000901	0	34·20	44·74	
0·02005	0·002762	0	34·18	44·65	
0·03844	0·009055	0	34·05	44·52	
0·04839	0·01338	0	34·18	44·54	A
0·05520	0·01550	0	—	—	
0·07554	0·02398	0	34·20	44·63	
0·09158	0·03051	0	34·05	45·17	
0·1408	0·04634	0	34·16	44·51	
0·1679	0·05128	—	42·58	32·26	A + B

Liquid phase, g.-mols./l.		Solid phase, %.			Com-
$Na_2C_2O_4$.	$Th(C_2O_4)_2$.	Na.	C_2O_4.	Th.	pound.*
0·1945	0·04420	11·70	45·39	29·31	
0·2281	0·03920	11·78	44·96	29·45	B
0·2879	0·03852	11·68	44·64	29·40	
0·3257	0·04543	—	57·16	10·43	
0·3184	0·03900	—	61·55	3·78	B + C
0·3110	0·03490	34·35	65·10	0·20	
0·3022	0·03036	—	65·50	0	
0·2793	0·01166	34·40	65·55	0	C
0·2672	0·00361	—	65·41	0	
0·2676	0	—	65·70	0	

* A = $Th(C_2O_4)_2,6H_2O$.   B = $Na_4Th(C_2O_4)_4,6H_2O$.   C = $Na_2C_2O_4$.

as the concentration of hydroxyl ions is increased nearly 10,000 fold, that of thorium ions must be appreciably reduced, probably by the formation of a complex anion, $Th(C_2O_4)_4''''$. The production of a higher p_H by the addition of alkali, or even ammonia, causes thorium hydroxide to be precipitated.

The second dissociation constant of oxalic acid is approximately 10^{-4}, from which it follows that, in order to form a soluble oxalate, a base must be capable of setting up a p_H of not less than 6. Clearly, this is impossible with so weak a base as thorium hydroxide. The fact that a well-defined thorium oxalate is formed must be attributed to its sparing solubility. As thoria is not precipitated until p_H 3·5 is reached, it appears that it should be capable of reacting with the first stage of oxalic acid, to give $Th(HC_2O_4)_4$, in a normal manner. (The fact that oxalic acid precipitates thorium oxalate prevents, however, such a reaction from taking place to any extent.) This would leave four hydrogen atoms, corresponding with the second stage of ionisation, free to react with stronger bases, such as the alkalis and ammonia, and so form salts of the type $Na_4Th(C_2O_4)_4$. Similar explanations may be advanced to account for salts with weak bivalent and tervalent bases, *e.g.*, $Na_2Cu(C_2O_4)_2$ (preceding paper) and $K_3Cr(C_2O_4)_3$ (Britton, J., 1926, 284). In solution these salts will primarily ionise to form the strongly electropositive ions, $Na^{\cdot}$, $K^{\cdot}$, and $NH_4^{\cdot}$, and the respective complex anions. The subsequent ionisation of the latter ions will be able to take place only if in the process the influence of the negative charges localised at one end of the ions can be overcome, and this is scarcely likely to occur when less electropositive metals are bound to the oxalate ions.