CHEMISTRY OF THE RARE EARTHS. PART VII. DISSOCIATION CONSTANTS OF THE THIOSULPHATES OF RARE EARTHS

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Dissociation constants of the thiosulphates of rare earths (La, Ce, Pr, Nd and Sm) have been measured. These values have been found to follow the "Serial Order" of the rare earths.

In a previous communication (Part VI, this *Journal*, 1949, 26, 405), the composition and isolation of several double thiosulphates of rare earths have been described. It has been shown there that the reactions between different alkali thiosulphates and rare earth salts take place in two steps, at first the simple thiosulphates $R_2(S_2O_3)_3$ are formed by the following reaction,

$$2R^{\cdots} + 3S_2O_3'' = R_2(S_2O_3)_3 . \qquad \ldots \quad (1)$$

and next double thiosulphates are formed having compositions $[R(S_2O_3)_4]''''$ and $[R(S_2O_3)_3]'''$ with sodium and potassium (also ammonium) thiosulphates respectively where R stands for La, Ce, Pr, Nd and Sm. The determination of dissociation constants of the simple thiosulphates forms the subject matter of the present communication.

Experimental

Dissociation constants have been determined by the method of continued variation of Job (*Compt. rend.*, 1928, 180, 928). The general principle of this method and the actual experimental procedure for the application of the same in this particular case have been described in Part VI of this series (*loc. cit.*).

In this method, Job has shown that the maximum composition "x" does not change when the concentrations of the two primary solutions used, are equimolecular. By maximum composition is meant the composition corresponding to the formation of the maximum amount of the compound in question. In other cases, that is, in cases where the concentrations are non-equimolecular, it varies and depends both upon the concentrations of two primary solutions and upon the equilibrium constant K for the reaction. Hence, the value of this maximum composition "x" determines with the help of the general equation of Job the equilibrium constant K.

For this purpose, the values of m and n, 2 and 3 respectively, as determined previously, are substituted in the general equation of Job,

$$K = \frac{C^{m+n-1} \times p^{n-1} \times \{(pm+n)x - n\}^{m+n}}{m^{n-1}.n^{m-1}.(p-1)^{m+n-1}\{n - (m+n)x\}} \qquad \ldots \quad (2)$$

when we get,

$$K = \frac{C^4.p^2[(2p+3)x - 3]^5}{12(p-1)^4(3 - 5x)} \qquad \ldots \qquad \ldots \quad (3)$$

Series of measurements are then carried out in the lines as with equimolecular solutions and from the respective curves drawn, the values of x, $i.$ $e.$ positions of maxima on the curves, are determined and substituted in equation (3).

The results are represented graphically in Figs. 1-5.

The values of C, the initial molar concentrations of the rare earth salts, taking complete dissociation at these dilutions, where molar concentrations are equal to ionic concentrations, $p=C'/C$, where C' is the initial molar concentration of the thiosulphate solution, and x being known, the dissociation constants have been calculated with the help of the equation (3) and these are shown in Tables I-V.

TABLE I

Dissociation constant of $La_2(S_2O_3)_3$.

Temp. $=32°\pm0.05°$.

	$C.$	$p.$	$x.$	$K.$	Ref.
1	0.025	4	0.35	1.28×10^{-9}	Fig. 1, curve I
2	0.01	10	0.27	2.64×10^{-9}	Fig. 1, curve II
3	0.01	4	0.42	2.04×10^{-9}	Fig. 1, curve III
4	0.01	2	0.535	2.44×10^{-9}	Fig. 1, curve IV

Mean 2.35×10^{-9}

TABLE II

Dissociation constant of $Ce_2(S_2O_3)_3$.

Temp. $=32°\pm0.05°$.

	$C.$	$p.$	$x.$	$K.$	Ref.
1	0.025	4	0.32	1.74×10^{-10}	Fig. 2, curve I
2	0.01	10	0.22	2.48×10^{-10}	Fig. 2, curve II
3	0.01	4	0.37	2.02×10^{-10}	Fig. 2, curve III
4	0.01	2	0.50	2.08×10^{-10}	Fig. 2, curve IV

Mean 2.08×10^{-10}

TABLE III

Dissociation constant of $Pr_2(S_2O_3)_3$.

Temp. $=32°\pm0.05°$.

	$C.$	$p.$	$x.$	$K.$	Ref.
1	0.02	5	0.27	2.72×10^{-11}	Fig. 3, curve I
2	0.01	4	0.34	2.81×10^{-11}	Fig. 3, curve II
3	0.01	5	0.30	3.21×10^{-11}	Fig. 3, curve III
4	0.01	2	0.48	3.36×10^{-11}	Fig. 3, curve IV

Mean 3.02×10^{-11}

TABLE IV

Dissociation constant of $Nd_2(S_2O_3)_3$.

Temp. $= 32° \pm 0.05°$.

	C.	p.	x.	K.	Ref.
1	0.02	5	0.265	1.36×10^{-11}	Fig. 4, curve I
2	0.01	4	0.33	1.21×10^{-11}	Fig. 4, curve II
3	0.01	5	0.29	1.42×10^{-11}	Fig. 4, curve III
4	0.01	2	0.47	1.05×10^{-11}	Fig. 4, curve IV
				Mean 1.26×10^{-11}	

TABLE V

Dissociation constant of $Sm_2(S_2O_3)_3$.

Temp. $= 32° \pm 0.05°$.

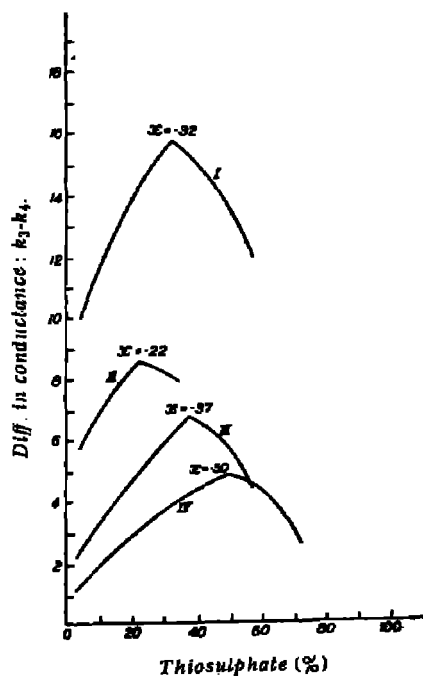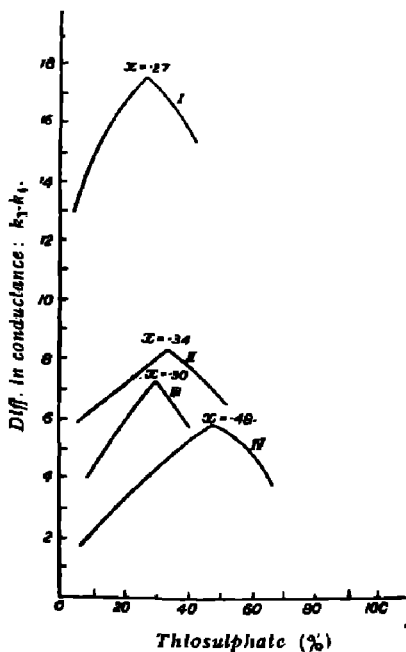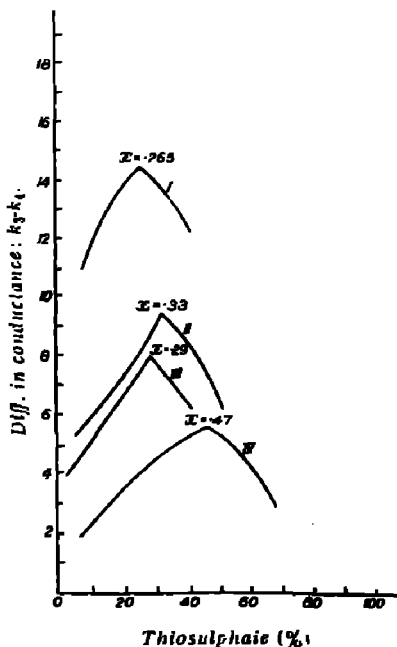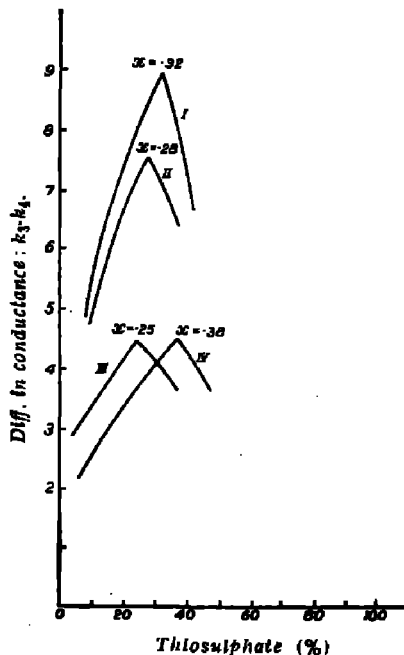|	C.	p.	x.	K.	Ref.
1	0.01	4	0.32	4.47×10^{-12}	Fig. 5, curve I
2	0.01	5	0.28	5.46×10^{-12}	Fig. 5, curve II
3	0.01	6	0.25	6.52×10^{-12}	Fig. 5, curve III
4	0.01	3	0.38	5.56×10^{-12}	Fig. 5, curve IV
				Mean 5.50×10^{-12}	

FIG. 1
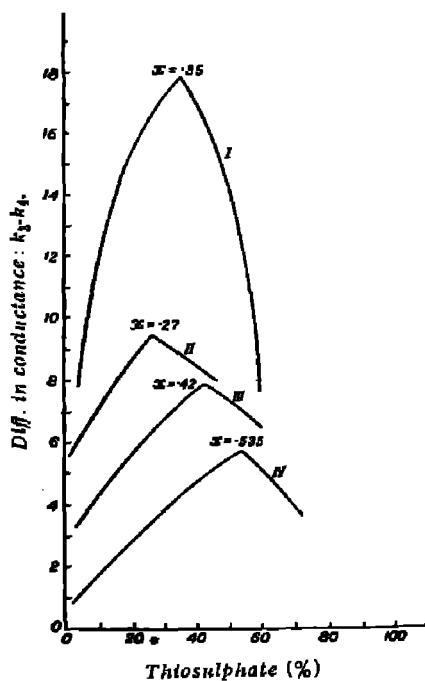
FIG. 2

FIG. 3

FIG. 4

FIG. 5

All measurements have been made in an electrically regulated thermostat capable of keeping the temperature constant with $\pm 0.05°$.

The values found for K, evidently shows that the stabilities of the salts follows the serial order of the rare earths as has been pointed out earlier.