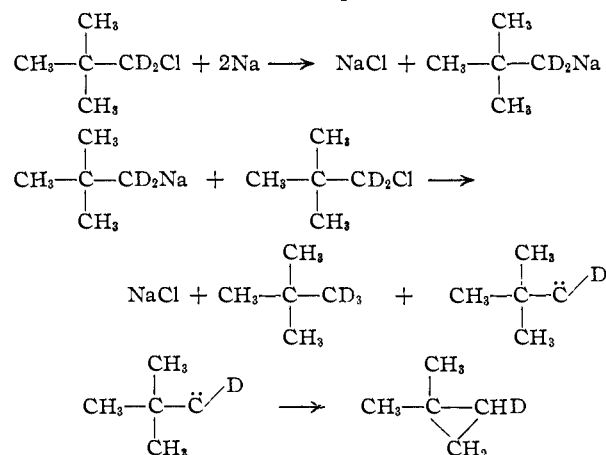


is not related to the above reaction, but represents conversion of neopentyl sodium or other intermediates, such as neopentyl radical, by reaction with moisture or the solvent.

A reasonable mechanism consonant with the close correspondence of yields of trideuterio-neopentane and monodeuterio-dimethylcyclopropane involves an  $\alpha$ -elimination step.



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#### THE ENTROPIES OF ASSOCIATION OF IONS

Sir:

It is the opinion of some workers that the entropy changes accompanying the association of ions in aqueous solution,  $\Delta S$ , are reasonably well understood<sup>1</sup> The changes usually are related to physical properties of the ions taking part or to their entropies of hydration,  $\Delta S_{\text{hyd}}$ . George,<sup>2</sup> in an analysis of a large number of data, recognized two types of behavior:

(1) For many ion pairs having one ion in common,  $\Delta S^0$  conformed to the empirical equation  $\Delta S^0 = -\Delta S_{\text{hyd}} + C$ , where  $C$  was a constant for each common ion. It was suggested that in these cases there was a loss of water of hydration and possible complex formation.

(2) Reactions for which  $\Delta S^0$  was independent of  $\Delta S_{\text{hyd}}$ . This was attributed to the formation of true ion pairs and was illustrated by data for

(1) R. J. P. Williams, *Ann. Reports Chem. Soc.*, **56**, 87 (1959).  
 (2) J. H. B. George, *J. Am. Chem. Soc.*, **81**, 5530 (1959).

bivalent metal sulfates. Unfortunately, George used the figures of Singh<sup>3</sup> for calcium, strontium, barium and lead sulfates and these are not association entropies at all but refer to entropy changes,  $\Delta S^1$ , for the reaction  $\text{MSO}_4(\text{solid}) \rightleftharpoons \text{M}^{2+} + \text{SO}_4^{2-}$ . Indeed it would be difficult to recognize ion association in solutions of salts as sparingly soluble as barium sulfate. Where comparison is possible, for calcium sulfate,  $\Delta S^1 = 26.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  whereas  $\Delta S^0 = 16.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .<sup>4</sup> Furthermore,  $-\Delta S_{\text{hyd}}(\text{Mg}^{2+})$  used by George,  $71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , differs from the calculated value  $63.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .<sup>5</sup>

More data now are available for bivalent metal sulfates and these are given in the table together with  $\Delta S_{\text{hyd}}(\text{M}^{2+})$  and calculated values of  $\Delta S_{\text{hyd}}(\text{MSO}_4)$ .

TABLE I  
 ENTROPIES OF ASSOCIATION AND OF HYDRATION

Reaction	$\Delta S^0$ (cal./deg. mole)	$-\Delta S_{\text{hyd}}(\text{M}^{2+})$ (cal./deg. mole)	$-\Delta S_{\text{hyd}}(\text{MSO}_4)$ (cal./deg. mole)	Ref.
$\text{Mg}^{2+} + \text{SO}_4^{2-}$	26.2	63.7	66	6
$\text{Ca}^{2+} + \text{SO}_4^{2-}$	16.1	50.2	62.5	4
$\text{Mn}^{2+} + \text{SO}_4^{2-}$	22.6	61.5	63	7
$\text{Co}^{2+} + \text{SO}_4^{2-}$	16.6	65	71	7
$\text{Ni}^{2+} + \text{SO}_4^{2-}$	21.7	66.5	67	7
$\text{Zn}^{2+} + \text{SO}_4^{2-}$	24.4	64	67	6

It is apparent immediately that  $\Delta S^0$  is not independent of  $\Delta S_{\text{hyd}}(\text{M}^{2+})$  and the second class of behavior suggested by George<sup>2</sup> cannot be substantiated.

(3) D. Singh, *J. Sci. Research Benares Hindu Univ.*, **6**, 131 (1955).

(4) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(5) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(6) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3706 (1958).

(7) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3934 (1959).

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 RECEIVED DECEMBER 15, 1960

#### RARE EARTH STANNATES, $\text{R}_2\text{Sn}_2\text{O}_7$

Sir:

Polycrystalline stannates of general formula  $\text{R}_2\text{Sn}_2\text{O}_7$ , isostructural with pyrochlore, where  $\text{R} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Lu}$ , have been prepared by solid state reaction from intimate mixtures of  $\text{R}_2\text{O}_3$  and  $\text{SnO}_2$ . The details of preparation are the same as given in a recent publication.<sup>1</sup>  $\text{Tb}_2\text{O}_3$  was prepared by heating the commercial oxide mixture in hydrogen at  $680^\circ$  for 2 hours and cooling to room temperature in hydrogen.

X-Ray diffraction investigations were made on powder samples with filtered copper radiation using both film and Geiger diffractometer techniques. Experimental lattice constants, determined as before,<sup>1</sup> are compared with calculated lattice constants in Table I. The latter were obtained from linear equations<sup>1</sup> using the rare earth radii of Templeton and Dauben.<sup>2</sup> All of the lanthanide stannates now have been prepared

(1) C. G. Whinfrey, D. W. Eckart and A. Tauber, *J. Am. Chem. Soc.*, **82**, 2695 (1960).

(2) D. H. Templeton and C. H. Dauben, *ibid.*, **76**, 5237 (1954).