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The Study of a System Involving Equilibrium between Inner Sphere and Outer Sphere Complex Ions: $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$

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The fractional conversion of $Co(NH_3)_5H_2O^{+++}$ to $Co(NH_3)_5SO_4^+$ at equilibrium is observed to be almost independent of the concentration of sulfate ion over a wide range above *ca.* 0.01 *M*. The behavior is understood if the aquo ion is assumed to be converted to a sulfate complex ion by outer sphere association at low concentration of sulfate ion. The interpretation is confirmed by observations on the ultraviolet absorption band of $Co(NH_3)_5H_2O^{+++}$ in the presence of varying amounts of sulfate ion. The change from the sulfato ion to the "isomeric" outer sphere complex ion is governed by the energy quantities: $\Delta H = -4.0 \pm 0.3$ kcal. mole^{-1}, $\Delta S = -13$ cal. deg.$^{-1}$ mole^{-1}. The reactions are first order in the concentration of Co(III). An increase in lability is observed with increase in sulfate ion concentration. The reactions are catalyzed by hydrogen ion. The activation energy for the change of the sulfato ion to the aquo ion is 19.3 ± 0.5 and for the reverse change is 23.7 ± 0.5 kcal. mole^{-1}.

In considering the structure in solution of a complex ion the stoichiometry of which has been established, the question arises as to its distribution between two forms, in one of which the addend is directly attached to the central ion occupying a position in the first sphere of coördination, and in the other occupying a position outside the first sphere of coördination. The latter type of structure can be expected to have considerable stability when the central ion has a high charge and when the addend is an ion of high charge. The importance of association of this type in water solution has been proven by the work of Davies,[1] Linhard[2] and Katzenellenbogen[3] using complex cations of the type $Co(NH_3)_6^{+++}$. Replacement of NH_3 by the anion does not take place under the conditions which were chosen and, in fact, the observations on the spectra[2] suggest that the first sphere of coordination is little disturbed in forming the outer sphere complex ions. It is evident that inert complex ions are extremely useful in defining the type of association under study, owing to the great difference in the speed at which association in the inner sphere and outer spheres takes place. For labile complex ions the distinction between the two types is much more difficult to make because the two forms are not readily separately characterized.

We have made use of an inert complex ion system also in our study. Substitution of water by water or other groups in $Co(NH_3)_5H_2O^{+++}$ takes place very slowly.[4] Our data with this cation and with $SO_4^=$ as an anion provide a dramatic demonstration of the presence in the solution of outer sphere complex ions, and furthermore, since H_2O and $SO_4^=$ are eventually exchanged, have made possible a comparison of the stabilities of inner sphere and outer sphere "isomeric" forms. The desirability of a more complete study of this system was indicated by work done on the water exchange reaction.[4] The experiments we are reporting supplement those described by Adell.[5] His study was limited to the range of dilute solutions ($(SO_4^=) \sim 10^{-2}$ or less) and therefore did not expose some of the interesting phenomena we have observed.

Experimental

The procedure was to follow the extinction of a solution containing initially the ion $Co(NH_3)_5SO_4^+$ or $Co(NH_3)_5H_2O^{+++}$ in an environment of known composition as a function of time. In all cases equilibrium was approached from both sides, and in every case the final values of the extinction agreed to within 1%. For numerous solutions the rate was followed as a function of time starting for a given environment both with the sulfato and the aquo ion. In every case tested the specific rates *k* (defined as below), forward and reverse, agreed to within 3% if only total sulfate were present in sufficient excess. The values of the initial optical densities for the sulfato and aquo forms, and of the final optical density make possible the calculation of the equilibrium quotient, and these data, together with the specific rate for approach to equilibrium, lead to the specific rate of aquotization and sulfato formation for each solution. The optical densities were measured using a Beckman spectrophotometer. The wave length 560 mμ at which the extinctions were measured lies on the long wave length side of a band with a maximum at 515 mμ for the sulfato and 495 for the aquo ion. The two maxima in the visible for the ions are not sufficiently well separated to make them useful in analyzing the solution. While the strong ultraviolet band does differ markedly for the two substances, light of longer wave length was preferred since it permitted the use of Corex cells. The extinctions of $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5SO_4^+$ at λ 560 mμ are changed somewhat (*cf.* Table I) as the environment changes, but only slightly as compared to the ultraviolet band. It was shown that the cobalt cations obey Beer's law in the solutions studied within experimental error. The extinctions change slightly with temperature—for example, there is an increase of *ca.* 3% in the extinction of the sulfato ion in 0.05 *M* Na_2SO_4 as temperature rises from 25 to 31°—hence for a series all extinction measurements were made at constant (±1°) temperature. In studying the variation of equilibrium constant with temperature the solutions which had been stored at different temperatures were all brought to the same temperature for comparison of optical densities. No significant readjustment in the inner sphere of coördination took place during the temperature change.

The substance $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ was the source of the sulfato ion. It was prepared as described by Jorgensen.[6] The content of Co and SO_4 were found to be 15.80% (theoretical, 15.79) and 51.42% (theoretical, 51.47). $Co(NH_3)_5H_2O(ClO_4)_3$ was prepared as described elsewhere,[4] and served as the source of the aquo ion. The agreement of final optical densities starting with both salts shows that the aquo salt was a sufficiently good preparation. Other reagents were of A. R. quality, used without further purification. Solutions were made up using redistilled water.

Conditions and Definitions.—In all experiments except expt. 11, Table I, the concentration of sulfate was in excess of the concentration of the complex ion by a factor of 8 or greater. Over the greater part of the range investigated, the specific rate as well as the equilibrium distribution is not very sensitive to the concentration of $SO_4^=$, and the initial recorded values which differ at most by 7 or 8% from the equilibrium values, serve as sufficiently good de-

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[1] C. W. Davies, *J. Chem. Soc.*, 2421 (1931).

[2] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1943).

[3] E. R. Katzenellenbogen, Paper No. 23, Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, September, 1950.

[4] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 823 (1952).

[5] B. Adell, *Z. anorg. allgem. Chem.*, **246**, 303 (1942).

[6] S. M. Jorgensen, *J. prakt. Chem.*, [2] **31**, 268 (1885).

TABLE I

DATA ON EQUILIBRIUM DISTRIBUTION AND RATE AS FUNCTION OF SULFATE CONCENTRATION

Temperature 31.1 ± 0.02°, except in expt. 8; $SO_4^=$ as Na_2SO_4 except in expts. 5 and 6

No.	$\Sigma[SO_4^=]$	$\Sigma[H^+]$	$k \times 10^4$	D_0^S	D	D_0^A	Q_e	$k_A \times 10^4$	$k_S \times 10^4$
1	2.90	0.30	11.3	0.491	0.328	0.213	1.42	6.6	4.7
2	1.15	.11	8.3	.495	.339	.214	1.25	4.6	3.7
3	0.57	.050	6.8	.501	.345	.213	1.18	3.7	3.1
4	.156	.015	4.8	.499	.345	.214	1.17	2.6	2.2
5	.156[a]	.015	4.3	.499	.347	.214	1.14	2.3	2.0
6	.156[b]	.015	5.2	.502	.348	.215	1.16	2.8	2.4
7	.052	.010	4.1	.506	.352	.214	1.12	2.2	1.9
8[c]	.052	.010	17.0	.506	.371	.214	0.86	7.9	9.1
9	.021	.010	3.4	.508	.345	.217	1.28	1.9	1.5
10	.0140	.010	2.8	.510	.341	.217	1.36	1.7	1.2
11[d]	.00216	.0061		.512	.321	.221	1.91		

[a] K_2SO_4. [b] $MgSO_4$. [c] Temperature 43.8°. [d] $(RSO_4HSO_4) = 0.00108$ *M*; $(HClO_4) = 0.005$ *M*. No other electrolyte.

scriptions of the sulfate concentration prevailing. Except where otherwise recorded, sulfate was introduced as Na_2SO_4.

$\Sigma[SO_4^=]$ refers to total $SO_4^=$ present, whether complexed or not (and differs but slightly from uncomplexed sulfate as noted above)

$\Sigma[H^+]$ represents concentration of H^+ present in all forms

R represents the radical $Co(NH_3)_5$

[A] represents the total concentration of species containing RH_2O^{+++}

[S] represents the total concentration of species containing RSO_4^+

D_0^S, D_0^A and D_∞ represent the optical densities ($\log I_0/I$) of solutions containing S initially, A initially and the equilibrium mixture, respectively. For all solutions, $cd = 0.0150$ cm. mole l.$^{-1}$.

k is the specific rate of change as measured in a plot of $\log |D_t - D_\infty|$ *versus* t. It is equal to the sum $k_A + k_S$ where these specific rates refer to the processes

$$S \xrightarrow{k_A} A$$
$$A \xrightarrow{k_S} S$$

Q_e represents the ratio [A]/[S] at equilibrium and is equal to k_A/k_S.

Specific rates are expressed with time in minutes.

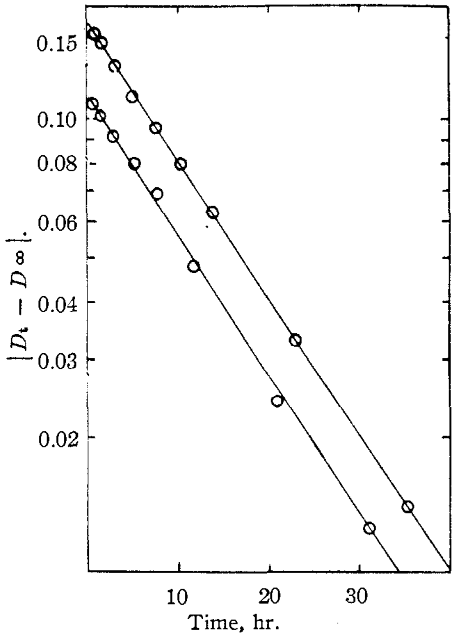

Fig. 1.—The variation of optical density with time medium, $\Sigma[SO_4^=] = 2.90$ *M*, $\Sigma[H^+]$, 0.3 *M*. Upper curve, sulfato salt approaching equilibrium; lower curve, roseo salt. D same for both.

Results

In Fig. 1 are presented typical data on the change of optical density with time, starting in one experiment with the aquo salt and in another with the sulfato salt.

Table I contains a summary of results obtained at relatively low acidity with $[SO_4^=]$ as the principal concentration variable. Acid was present in all solutions to suppress the acid dissociation of RH_2O^{+++}. The results reported later show that (H^+) (or (HSO_4^-)) is not an important variable at the levels used in the series in Table I.

Table II is a summary of the data obtained on the variation of Q_e with temperature. The data are shown plotted in Fig. 2 to yield values of ΔH in kcal./mole which are as follows for the change: S → A.

TABLE II

VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

Medium		Q_e at		
$\Sigma[SO_4^=]$	ΣH^+	24.9°	31.1°	43.8°
2.90	0.30	1.67	1.42	1.11
0.052	.010	1.28	1.12	0.86
0.021	.010	1.44	1.27	1.01

$$-4.1 \pm 0.3 \text{ at } 2.6\ M\ SO_4^=$$
$$-4.0 \pm 0.3 \text{ at } 0.052\ M\ SO_4^=$$
$$-3.6 \pm 0.3 \text{ at } 0.021\ M\ SO_4^=$$

Table III presents data obtained for solutions containing also sodium perchlorate, Table IV for solutions with varying amounts of $NaHSO_4$ and Table V for solutions with varying amounts of $NaHSO_4$ and H_2SO_4. In Table VI some data dealing with the changes in extinction for the ultraviolet band of RH_2O^{+++} as $SO_4^=$ is added, are presented. The study of the spectra in solutions of various compositions is itself a major undertaking and more complete data for this and related systems will be presented in a future publication.

Discussion

The most interesting feature of the equilibrium data is that the ratio Q_e is almost independent of $(SO_4^=)$ over a wide concentration range, extending from 0.02 to 2.6 *M*. It is further remarkable that this ratio instead of diminishing at high $(SO_4^=)$, in fact shows a slight increase in this concentration region. These observations suggest that the principal equilibrium operating over the range studied is

$$RSO_4^+ + H_2O \overset{K_I}{\rightleftharpoons} RH_2O^{+++}\cdot SO_4^= \qquad (I)$$

If ion pair formation is essentially complete even at 0.02 *M* $SO_4^=$ the change S to A involves species of the same stoichiometry with respect to Co(III) and $SO_4^=$ and hence also of the same charge. Therefore the effects of salts, including $SO_4^=$, is expected to be relatively slight. In the region of

TABLE III

THE INFLUENCE OF NEUTRAL ELECTROLYTE

Temperature 31.1°

No.	$\Sigma[SO_4^=]$	$\Sigma[H^+]$	$(NaClO_4)$	$k \times 10^4$	D_0^S	D_0^A	Q_e	$k_A \times 10^4$	$k_S \times 10^4$
1	0.021	0.010	0.93	1.92	0.516	0.225	4.40	1.57	0.355
2[a]	.054	.010	.71	2.56	.511	.223	2.13	1.74	0.82
3	.156	.010	.54	4.38	.506	.218	1.28	2.46	1.92
4	.054	.010	2.00	2.04	.524	.226	2.68	1.49	0.554
5	.156	.010	1.70	2.68	.507	.218	1.39	1.56	1.12

[a] The series was planned at constant μ, but insufficient $NaClO_4$ was inadvertently added in this experiment.

TABLE IV

THE INFLUENCE OF BISULFATE ION

Temperature 31.1°

No.	(Na_2SO_4)	$(NaHSO_4)$	$(NaClO_4)$	$k \times 10^4$	D_0^S	D_0^A	Q_e	$k_A \times 10^4$	$k_S \times 10^4$
1	0.054	0.10	0.60	3.61	0.506	0.215	1.47	2.1	1.5
2	.054	.30	.40	4.62	.500	.215	1.35	2.6	2.0
3	.054	.70	.00	6.34	.499	.214	1.44	3.7	2.6
4	.54	.10	1.40	5.25	.503	.224	1.07	2.7	2.5
5	.54	.40	1.10	5.85	.500	.219	1.13	3.3	2.6
6	.54	1.50	0.00	9.02	.500	.214	1.42	5.4	3.6

TABLE V

RATE AND EQUILIBRIUM DATA FOR SOLUTIONS CONTAINING $NaHSO_4$ AND H_2SO_4

Temperature 31.1°

No.	$(NaHSO_4)$	(H_2SO_4)	$k \times 10^4$	D_0^S	Q_e	$k_A \times 10^4$	$k_S \times 10^4$
1	0.00	3.00	16.1	0.488	2.87	11.9	4.2
2	1.00	2.00	12.5	.496	2.14	8.5	4.0
3	3.00	0.00	10.2	.496	1.61	6.3	3.9
4	0.00	6.00	27.5	.485	2.26	19.1	8.4
5	3.00	3.00	21.0	.488	1.94	13.9	7.1
6	5.00	1.00	18.5	.490	1.69	11.6	6.9
7	0.00	9.00	36.0	.460	1.40	21.	15.

TABLE VI

THE ULTRAVIOLET EXTINCTION COEFFICIENTS OF $Co(NH_3)_5H_2O^{+++}$ AT VARIOUS CONCENTRATIONS OF SULFATE ION

Temperature 27 ± 1°; $\epsilon = 1/cd \log I_0/I$ in l. mole $^{-1}$ cm.$^{-1}$; $(RH_2O(ClO_4)_3) = 8.0 \times 10^{-4}\ M$; $(HClO_4) = 0.01\ M$

	ϵ at $\Sigma(SO_4^=)$				
λ in mμ	0.000	0.0062	0.0125	0.0416	0.1040
270	15	26	34	42	44
260	31	76	89	112	118
250	143	257	288	338	360
245	336	503	538	613	650
240	762	990	1010	1120	1180
235	1620	1910	1940		

low sulfate ion concentration the equilibrium

$$RH_2O^{+++} + SO_4^= \overset{K_{II}}{=} RH_2O^{+++}\cdot SO_4^= \quad (II)$$

presumably becomes important and RH_2O^{+++} as well as $RH_2O^{+++}\cdot SO_4^=$ contributes to [A]. At high concentration of $SO_4^=$, Q_e will be altered by salt effects on equilibrium (I) or by further association of sulfate with the complex ions. However, the affinities of $RH_2O^{+++}\cdot SO_4^=$ and RSO_4^+ for sulfate ion appear to be about the same, since Q_e changes only slightly even at high sulfate concentration.

The conclusion that RH_2O^{+++} and $SO_4^=$ are strongly associated is supported by Davies' calculations[1] for the similar system $Co(NH_3)_6^{+++}$ and $SO_4^=$ which yielded 3.3×10^3 as the equilibrium constant for the association reaction at zero ionic strength and 25°. The conclusion is directly proven by the data in Table VI on the ultraviolet extinctions of RH_2O^{+++} in the presence of varying concentrations of $SO_4^=$. Marked changes in the extinction are observed in the ultraviolet band, with the extinctions at 240 and 235 mμ approaching saturation values when $(SO_4^=)$ is only $6 \times 10^{-3}\ M$. More complete data will be required to obtain values of equilibrium con-

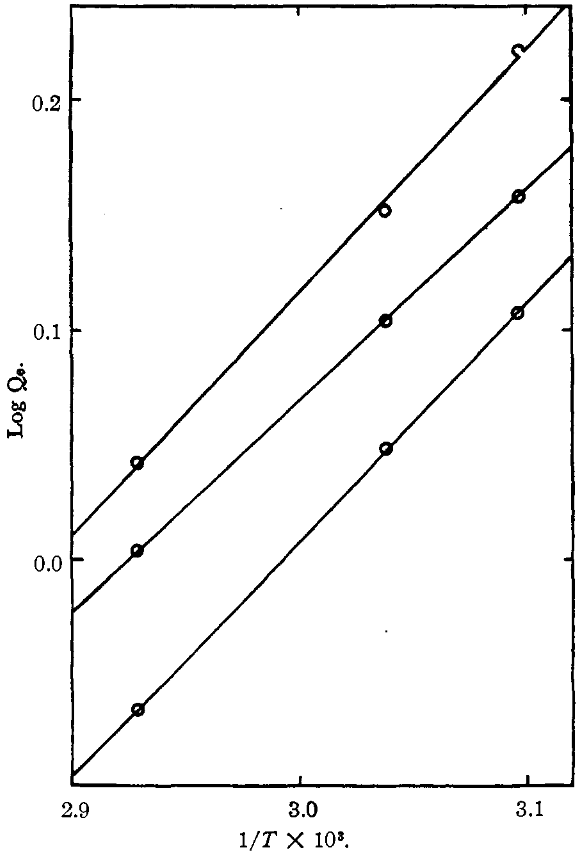

Fig. 2.—The variation of Q_e with temperature. Curves are in order for 2.90, 0.021 and 0.052 M, $\Sigma[SO_4^=]$ reading from top to bottom.

stants, particularly because successive stages of association apparently must be taken into account. This is evidenced by the observation that the rate of approach to saturation extinction values is different at different wave lengths.

If the assumption is made that the ratio $(RH_2O^{+++}\cdot SO_4^=)/(RSO_4^+)$ remains constant below 0.05 M $SO_4^=$, and is measured by the ratio Q_e at this sulfate ion concentration, the value of K_{II} for expt. 11 is calculated as 1.1×10^3. When corrected for the difference in μ, this value will be close to that reported by Davies for $Co(NH_3)_6^{+++}$ and $SO_4^=$.

The measured heats of reaction on the interpretation suggested apply to reaction I. It should be noted that the change is exothermic. It is interesting that the heat of transfer of $SO_4^=$ from inner sphere to outer sphere does not change appreciably as $(SO_4^=)$ changes from 0.05 to 2.6 M. The decrease in $|\Delta H|$ at lower $(SO_4^=)$ can be attributed to participation by equilibrium (II). Using the observed values of equilibrium constant and ΔH at 0.05 M $SO_4^=$, ΔS at this concentration of sulfate is calculated as -13 e.u. An entropy decrease can be expected since ions of opposite charge are separated in transferring $SO_4^=$ from inner sphere to outer sphere, thus increasing the interaction with the solvent.

The effect of $NaClO_4$ on the equilibrium $[A]/[S]$ is presumably largely in increasing the concentration of RH_2O^{+++} relative to $RH_2O^{+++}\cdot SO_4^= + RSO_4^+$. There may also be an effect on the ratio $(RH_2O^{+++}\cdot SO_4^=)/(RSO_4^+)$, but this is impossible to decide from the data. Assuming that the ratio is unaltered by $NaClO_4$ and is given by the value of Q_e at 0.05 M $SO_4^=$, the quotient K_{II} for expt. 1, Table III is calculated as 16, and for expt. 2 of the same table, at somewhat lower ionic strength as 20. The large change in K_{II} from the conditions of expt. 11 to those obtaining in the experiments of Table III, is in line with the large value of Δz^2 for reaction (II).

The data of Table IV suggest that salts do affect the ratio $(RH_2O^{+++}\cdot SO_4^=)/(RSO_4^+)$. While in dilute solution (expts. 1, 2, 3, Table IV) $NaClO_4$ and $NaHSO_4$ influence Q_e in approximately the same way, in more concentrated solution (expts. 4, 5, 6) replacing $NaClO_4$ by $NaHSO_4$ enhances the ratio. For concentrated electrolyte solutions effects due to changes in the activity of water must become important. The decrease in Q_e as the concentration of sulfuric acid is increased is attributable, in part at least, to this cause.

Over the composition range investigated, which includes variation of the initial concentration of Co(III) from 0.0150 to 0.00150 as well as the variation in concentrations of other ions, the reactions are first order in (Co(III)). Using solutions at lower $(SO_4^=)$ than we have in our rate study, Adell[6] observed k_A to be independent of $SO_4^=$, and k_S to be given by an expression of the form $k^0\,f(SO_4^=)\,(RH_2O^{+++})$, where f is a function taking account of interionic attraction effects. For the conditions we have adopted, RH_2O^{+++} is almost completely associated with $SO_4^=$, so that the net change (except for further association of Co(III) and $SO_4^=$) is represented in equation (I). The data of Table I exhibit the interesting feature that k_A and k_S are about equally affected by the concentration of sulfate ion for solutions in which Co(III) can be presumed to be almost completely associated with $SO_4^=$. The catalytic effect of sulfate ion is best demonstrated by observing its effect on k_A for solutions at constant ionic strength. Comparison of expts. 1, 2 and 3 of Table III shows that $SO_4^=$ increases the rate of removal of $SO_4^=$ from the inner coördination sphere. Catalysis by anions of substitution reactions in complex ions has been observed in other cases.[7,8]

The two series of experiments in Table IV show the influence of H^+ in increasing the lability of the system. The effect is attributable specifically to H^+ rather than HSO_4^-, since it decreases as $(SO_4^=)$ increases. The specific effect of H^+ is not great (and is not expected to be great since the H^+ has only a slight affinity for $SO_4^=$), and did not appear over the variation in (H^+) executed by Adell[6] in dilute electrolyte solution. The differences in lability observed for solutions containing K^+, Na^+ and Mg^{++} are probably significant, and indicate increasing interaction between cation and $SO_4^=$ in the order presented. The results in very acidic solution show general trends which are consistent with the ideas presented. It may be noted in addition, that the relatively slight increase in k_A from 6.0 M H_2SO_4 to 9.0 M H_2SO_4 is attributable to the decrease in activity of the water.

Comparison of the specific rates at the two temperatures leads to values of E and Q at 0.05 M $SO_4^=$ corresponding to k_A and k_S of 19.3 ± 0.5 and 23.7 ± 0.5 kcal./mole, and 10^{10} and $10^{13.5}$ l. mole^{-1} min.$^{-1}$. The change from $RH_2O^{+++}\cdot SO_4^=$ to RSO_4^+ has a normal frequency factor and the over-all entropy change must appear in the entropy of activation for the reverse change. This implies that the charge separation in the activated state is closer to that in $RH_2O^{+++}\cdot SO_4^=$ than it is in RSO_4^+. This in turn is more in line with an activated state of coördination number 5 rather than with one of 7.[4]

An original purpose in undertaking the kinetic investigation of the present system was to attempt to distinguish S_N1 and S_N2 mechanisms on the basis that at high $SO_4^=$, a limiting rate would be expected (governed by the rate of formation of a presumed intermediate, such as $Co(NH_3)_5^{+++}$ for the S_N1 mechanism, whereas on the S_N2 mechanism, such a limiting rate would not be expected. The effort to make such a distinction on kinetic evidence is vitiated however by the association of RH_2O^{+++} and $SO_4^=$ which, in effect, changes the nature of the reactants. However, in view of the demonstrated effect of $SO_4^=$ in increasing lability of the system, the observation that the rate of water exchange is diminished when it occurs in the presence of the net change to RSO_4^+ becomes stronger evidence for an important contribution by the S_N1 mechanism.[4]

Various comparisons which can be made makes it seem likely that the observations recorded here on

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[7] F. J. Garrick, *Trans. Faraday Soc.*, **34**, 1088 (1939).

[8] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

the equilibrium between inner sphere and outer sphere complex ions will find their counterpart in labile systems of the same charge type, as for example Fe^{+++}–$SO_4^=$ and Ce^{+++}–$SO_4^=$. In general the equilibrium behavior of $Co(NH_3)_5H_2O^{+++}$ in association reactions with anions is very nearly the same as for other tripositive ions forming 1:1 complexes. Thus, the equilibrium constant for association with Cl^- at 25° and $\mu = 0.05$ is 4.1[9] and the association reaction is slightly endothermic. This behavior is in striking similarity to that of Fe^{+++}–Cl^-.[10] Furthermore, for $Co(NH_3)_5^{+++}$ the affinities decrease in order from Cl^- to I^-, as they do for Fe^{+++}. The association constant observed[11] for La^{+++} and $SO_4^=$ at $\mu = 1.00$ and 25° is 25 and for Ce^{+++} and $SO_4^=$ under the same conditions is 17.5.[12] In the present system in the same salt environment (but at 31.1°) the constant for association involving outer sphere complexes is only 16, and if the inner sphere complexes are included, the constant would be roughly doubled. These similarities strengthen the view that for the labile systems consisting of $SO_4^=$ and tripositive ion, the ratio of concentrations of inner and outer sphere forms will also be of the order of magnitude of unity.

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[9] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937).

[10] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[11] K. L. Mattern, Thesis, University of California, Berkeley, 1951.

[12] T. W. Newton, private communication.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XIV. Heat Capacity of Sodium Borohydride from 15–300°K.[1]

BY HERRICK L. JOHNSTON AND NATHAN C. HALLETT

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The heat capacity of sodium borohydride has been measured from 15 to 300°K. and the thermodynamic functions have been calculated. A second-order transition, with an entropy of 1.22 e.u. occurs at 189.9°K. The entropy at 298.16 is 24.26 e.u.

Introduction

The first low-temperature heat capacity data for sodium borohydride were obtained by Boodman, Stegeman and Mason[2] for the temperature range 55–298°K.

During the present investigation, the heat capacities and thermodynamic functions have been measured in the range 15–300°K., in order to extend the earlier measurements.

Apparatus

The heat capacity measurements were made in calorimeter No. 7, one of a group of seven calorimeters for the measurement of the heat capacity of solid materials. This calorimeter is identical in all respects to calorimeter No. 1 which has been described in an earlier paper.[3]

The sample of sodium borohydride was obtained through the courtesy of the General Electric Research Laboratory at a reported purity of approximately 87%. The sample was purified and analyzed by the method of Davis, Mason and Stegeman[4] resulting in a purity of 99.60%. All handling of the sample, including filling, sealing and emptying the calorimeter was done under anhydrous conditions in a dry-box. The calorimeter contained 26.0530 g. (0.68835 mole) of sodium borohydride.

Experimental Results

The heat capacity data, as shown in Table I and in Fig. 1, follow a normal curve from 15°K. to about 169°K. at which point a second-order type transition occurs and the apparent heat capacity rises from about 16 calories/mole/degree to over 100 calories/mole/degree. From 193.5°K. to room temperature the heat capacity again follows a normal curve.

Below 30°K. the heat capacities followed the T^3 law so that it was possible to evaluate the region below 15°K. using the equation

$$C_v = 4.90 \times 10^{-5}T^3$$

Three determinations were made to obtain an accurate value for the heat of transition. The average value obtained (see Table II) is 635.3 calories per mole for the total enthalpy change from 169–193.5°K., which corresponds to an entropy change of 3.35 e.u. By subtracting the area between 169–193.5°K. under the extrapolated portion of the normal capacity curve (Fig. 1) a value of 232.6 calories/mole was obtained for the heat of transition and a corresponding value of 1.22 e.u. for the transition entropy increase. This value is 0.22 e.u. higher than the value of 0.99 e.u. given by Boodman, Stegeman and Mason.[2] This is understandable, however, since their heat of transition was evaluated by a method used by Giauque and Wiebe.[5] The boundaries of transition were arbitrarily set as those points where the heat capacity became 0.500 calorie/gram/degree (18.924 calories/mole/degree). Since there is an apparent "pre-heat of transition" below the 0.500 calorie/gram/degree, their results would be lower than those of this research.

The values for the entropy and enthalpy (Table III) were obtained from large scale graphs of C_p/T *versus* T and C_p *versus* T, respectively, with the aid of Simpson's rule.

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[2] D. Boodman, G. Stegeman and L. Mason, Thermal Properties of some Hydrides, Univ. of Pitts., ONR Contract Number N6 ori 43, T.O.I. Technical Report, Oct. 10, 1949.

[3] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

[4] W. D. Davis, L. S. Mason and G. Stegeman, *ibid.*, **71**, 2775 (1949).

[5] W. F. Giauque and R. Wiebe, *ibid.*, **50**, 2193 (1928).