sites in the metal and in which the hydrogen has exceptionally low energy. Experiment shows[9] that the solvent power of a metal for hydrogen is enhanced by cold working. This undoubtedly results from the retention of atypical sites in the deformed metal which are energetically more favorable for hydrogen than those in the ideal lattice. Clearly no metal will be entirely free of such effects. Atypical sites will exist in any disturbed region in the lattice-at grain boundaries, along dislocations, adjacent to impurities, etc.

With this viewpoint in mind the following sequence of events may be postulated. As the vanadium is hydrogenated, the low-energy, atypical sites will tend to be occupied first. This will lead to a higher than "normal" heat of vaporization at high dilutions. However, as the amount of hydrogen is increased, the atypical sites become saturated and hydrogen will begin to enter the usual lattice sites and the normal trend for the heat of vaporization sets in. Of course, when there is preferential occupancy of sites, this is at the expense of the entropy of the system and will tend to be discouraged the higher the temperature. For this reason and also because the importance of the heat of vaporization in comparison with the entropy of vaporization diminishes as temperature increases, the maxima in the isotherms in Fig. 1 are expected to become less pronounced the higher the temperature. This expectation is borne out by experiment.

These considerations are, of course, relevant to the extrapolation procedure used to evaluate the thermodynamic properties of the system. They suggest that if data for the dissolving of hydrogen in "ideal" vanadium were desired, extrapolation should be made without regard to the fall in $\sqrt{P}/N_H$ at the highest dilutions. It is not exactly clear how one would make such an extrapolation but regardless of how this might be done, it appears that the thermodynamic properties so computed would not differ greatly from those obtained in the present work, except for the most dilute solutions.

Another idea has been advanced to account for deviations from Sieverts' Law such as have been observed for the present system at hydrogen concentrations between 2 and about 25 atomic %. For the Pd–H and Zr–H systems the negative departures from Sieverts' Law have been attributed to attractive interactions between neighboring hydrogen atoms and these systems have been treated on this basis by statistical mechanical methods by Lacher[10] and Rees.[11] If the attractive interactions are the dominant factor, one expects a clustering of solute atoms at low temperatures. The tendency for clustering is of course reduced as the temperature increases with the result that deviations from ideality are diminished correspondingly. Concurrently the destruction of the clusters produces a decrease in the heat of vaporization. Thus if the negative deviations originate with attractive interactions, one expects a significant change in the heat of vaporization with temperature, provided that the temperature range covered is large enough to produce an appreciable change in the magnitude of the observed deviations. This condition is fulfilled in the present study and the data show that within the limit of experimental error the heat of vaporization is invariant with temperature. Furthermore, if the solute atoms interact attractively, one expects the strongest dependence of heat of vaporization on composition to occur in the most concentrated solutions. Actually the converse is found to be the case. The heat of vaporization begins to level off when N_H is increased above about 0.25. Thus the observed behavior does not seem to be in accordance with that expected if attractive interactions between hydrogen atoms were the predominant factor.

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(9) D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1948, p. 21.

(10) J. R. Lacher, *Proc. Roy. Soc.* (*London*), **A161**, 525 (1937).

(11) A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 335 (1954).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

Thermodynamics of the Sulfate Complexes of Thorium[1]

BY A. J. ZIELEN

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By use of the cation-exchange resin technique in perchloric acid solutions at an ionic strength of 2.00 and 25°, thorium(IV) was observed to associate with sulfate according to the stepwise reactions: $Th^{+4} + HSO_4^- = ThSO_4^{+2} + H^+$ and $ThSO_4^{+2} + HSO_4^- = Th(SO_4)_2 + H^+$ with the association constants $K_1 = 166 \pm 8$ and $K_2 = 21.7 \pm 1.5$. The heats and entropy changes of the reactions were determined calorimetrically with the results: ΔH_1 and ΔH_2 equal -0.54 ± 0.05 and -0.89 ± 0.08 kcal./mole, respectively and ΔS_1 and ΔS_2 equal 8.4 ± 0.2 and 3.2 ± 0.3 cal. deg.$^{-1}$ mole^{-1}, respectively. The heat of ionization of bisulfate ion at an ionic strength of 2.00 and 25° was also measured calorimetrically with the result ΔH equals -5.54 ± 0.17 kcal./mole.

Introduction

The complexing of aqueous thorium by inorganic ligands has received considerable attention in recent years,[2] but certain aspects have been neglected. A cursory examination of the literature has failed to reveal a single determination of the heats and entropies of complexing, and in addition nearly all complexing constants have been determined by

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949); (b) R. A. Day and R. W. Stoughton, *ibid.*, **72**, 5662 (1950); (c) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951); (d) W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952); (e) V. V. Fomin and E. P. Maiorova, *Zhur. Neorg. Khim.*, **1**, 1703 (1956).

the benzene–thenoyltrifluoroacetone (TTA) technique. Thus it appeared desirable to employ an independent procedure as a check on the TTA extraction method and to combine the association constants so obtained with a calorimetric determination of the heats of complexing.

The determination of complexing constants by cation exchangers has been well developed by Fronaeus[3] and successfully employed in a number of systems. Due to extremely strong sorption on the resin, application of the method to a tetravalent ion presented certain experimental difficulties but in turn led to simplifications in treatment of the data. The final results indicate that the cation exchange technique should be generally applicable to the complex ion chemistry of thorium.

Experimental

Cation-exchange Studies.—Distribution of thorium between the resin and solution phases was measured at constant thorium load on the resin as a function of varying sulfuric acid concentration. Two main series of experiments were carried out—the first at an equilibrium hydrogen ion concentration of 2.000 M (perchloric and sulfuric acids) and the second at equilibrium hydrogen and sodium ion concentrations each of 1.000 M (perchloric acid–sulfuric acid–sodium perchlorate). These concentrations were calculated on the basis of the make-up solutions and took into account small corrections due to the resin swelling factor and the dissociation of bisulfate.

The thorium concentration of solutions was measured radiometrically by use of tracer Th-234 (UX$_1$) added to Th-232. Experiments employing carrier free UX$_1$ yielded erratic results undoubtedly due to adsorption on glass and resin surfaces. Since only a small fraction of the initial activity remained in solution after contact with the resin, it was necessary to run counting determinations on a large sample. This was accomplished by use of a thin wall G–M tube especially designed for direct immersion in the radioactive solution (Mark 1, Model 81, Radiation Counter Laboratories, Inc.).[4] Geometry calibrations with standard uranyl nitrate solutions indicated that 6.4% of all 2.32 mev. betas from UX$_2$ (1.1 min. Pa-234 daughter of UX$_1$) were counted for 6.7-ml. samples.

In each experiment 0.1 g. of resin and 8 ml. of appropriate sulfate solution were introduced into a 10-ml. stoppered erlenmeyer flask. A 0.300-ml. aliquot of tracer thorium then was added by means of a 1 ml. Gilmont Ultramicroburet. The initial concentration of carrier thorium in the resulting solution was about 10^{-5} M. The flask was sealed, inserted in a special rubber container and agitated in a water-bath thermostated at 25.0 ± 0.1° for a minimum period of 48 hr. Resin and solution phases were then quickly separated by passage through a sintered glass filter, and either direct or appropriately diluted 6.7-ml. samples of the solution were assayed for thorium radiometrically. Sufficient counts were obtained on each sample for a statistical standard deviation of 1% or less. All counting rates were corrected for the calibrated coincidence loss of the G–M tube and were then normalized to the same zero time on the basis of the 24.10 day half-life of UX$_1$.[5]

Calorimetry.—After a number of minor modifications a twin calorimeter originally designed by Hatcher[6] for a determination of the disintegration energy of tritium was employed in this work. The calorimeter proper consists of two soft glass commercial Thermos flasks of about 218-ml. capacity. In operation the Dewar flasks are rigidly mounted and completely immersed in a water-bath thermostated to ± 0.01°. The flasks are sealed water tight by rubber stoppers under the pressure of thumb screws. Three inlet tubes of Monel metal are permanently mounted in each stopper and provide housing for electrical heater, difference thermocouple and the centrally located stirring shaft. The difference thermocouple consists, at each end, of 24 junctions of #38 copper and #30 constantan encased in thin wall gold tubing. The thermocouple gives approximately 1000 microvolt/degree and has a resistance of 127 ohms. The heaters each consist of about 94 ohms of #40 double glass insulated Manganin in double layer helical bifilar winding encased in thin wall gold tubing. The heaters are provided with both voltage and current leads to provide an accurate measurement of the resistance under working conditions.

Both stirring shafts are actuated by the same sprocket chain driven by a small synchronous motor. By a simple mechanical eccentric the resultant motion of the shafts is alternate rotation of 360° in opposite directions at a rate of 135 reversals/min. Each stirring shaft proper is a stainless steel rod encased in Monel tubing with agitation provided by small platinum paddles attached near the end. Reactant solutions (generally about 5 ml.) were introduced into the calorimetric solution by smashing fragile glass bulbs waxed to the end of the stirring shaft against a small glass anvil mounted on the base of the Dewar flask. For this purpose the stirring shafts were designed to allow a small amount of independent vertical movement.

In this research the calorimeter was not employed as a twin system. One Dewar flask was filled with water taken directly from the thermostated bath and merely served as a convenient reference point for the difference thermocouple. The thermocouple output was measured with a Rubicon Six-Dial Thermofree Potentiometer conjunctive with a Model 14 Liston-Becker d.c. Breaker Amplifier and Varian Associates Model G-10 Graphic Recorder combined to serve as a null point indicator. The over-all performance of the equipment readily allowed detection of potential changes of 0.01 microvolt. Since the relative heat capacity of the charged calorimeter is about 0.2 cal./microvolt, this would apparently place the accuracy of a heat measurement at ±0.002 cal. However, errors introduced by the variable heat effects in breaking the sample bulb place the limiting uncertainty under favorable conditions at about ± 0.01 cal.[7]

In each calorimetric run weighed amounts of component stock solutions were added to the Dewar flask and sample bulb, giving a final solution volume of 200 ml. After an equilibration period of 2 or 3 hours, heats of reaction were measured at 25.0 ± 0.1° using electrical heating to calibrate the heat capacity of the system immediately before and after breaking the sample bulb. To convert concentrations to the moles/l. scale, the density of the final solution was determined by weighing aliquots taken with a calibrated pipet. All heats are reported in terms of the defined calorie (1 cal. = 4.1840 abs. joules).

As a final check on the apparatus the heat of ionization of water was measured by adding 0.1 M sodium hydroxide (sample bulb) to a slight excess of hydrochloric acid. Correcting to standard state conditions with the appropriate heats of dilution,[8] two runs each with an observed heat between 7 and 8 cal. gave values for $\Delta H°$ of 13.342 and 13.335 kcal./mole. The close check is probably somewhat fortuitous but in satisfactory agreement with the literature value of 13.360 kcal./mole.[8]

Materials.—Macro level stock solutions of thorium perchlorate were prepared by repeated fumings of reagent grade thorium nitrate in excess perchloric acid. The thorium content was determined by precipitation of the hydroxide and ignition to ThO$_2$. The amount of excess perchloric acid was measured by passing samples through a cation exchanger column (Dowex-50, hydrogen ion form) and titrating with standard base.

The UX$_1$ for each series of experiments was obtained by treating 1.3 kg. of uranyl nitrate hexahydrate with 1.5 l. of ether. The aqueous phase was drawn off, carrier thorium added and extracted with 0.5 M TTA in benzene. The benzene phase was scrubbed repeatedly with 0.1 M perchloric acid (9 or 10 times) until spot tests with sodium ferrocyanide indicated the aqueous phase free of uranyl ion. The TTA cycle was then repeated by extracting into 2 M perchloric

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[3] S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951); **6**, 1200 (1952); **7**, 21 (1953); *Svensk Kem. Tidskr.*, **64**, 317 (1952); **65**, 19 (1953).

[4] For a good description of the use of a similar G–M tube see J. Rydberg, *Acta Chem. Scand.*, **4**, 1503 (1950).

[5] G. B. Knight and R. L. Macklin, *Phys. Rev.*, **74**, 1540 (1948).

[6] J. B. Hatcher, unpublished data, this Laboratory.

[7] Six runs to measure the heat of breaking sample bulbs filled with distilled water into distilled water gave a mean and standard deviation of 0.039 ± 0.009 cal. evolved. A discussion of the uncertainties in the heat effects involved is presented by W. P. Hutchinson and A. G. White, *J. Sci. Instr.*, **32**, 309 (1955).

[8] "Selected Values of Chemical Thermodynamic Properties." National Bureau of Standards, Circular 500 (Feb. 1952).

acid, precipitating the hydroxide, dissolving the precipitate in 0.1 *M* perchloric acid and extracting again with benzene–TTA. After 3 final scrubs with 0.1 *M* perchloric acid, the tracer stock solution was obtained by extraction into 2 *M* perchloric acid followed by two benzene scrubs to remove traces of TTA. Observations on the activity of a sample of this tracer carried out over a 45-day period indicated the half-life to be 24.2 ± 0.1 days (least squares with standard deviation) in good agreement with the literature value.[5] The over-all yield of UX_1 initially in secular equilibrium with the U-238 was about 70%.

The cation exchanger employed was Analytical Grade AG 50-X12 processed from Dowex-50 by Bio Rad Laboratories, 200–400 mesh, capacity 5.0 meq./g. of dried resin. For the experiments in 2 *M* hydrogen ion the resin was repeatedly treated with a large excess of 2.000 *M* perchloric acid, thoroughly washed with water and dried at 45°. A mixed sodium–hydrogen ion form of the resin was prepared for the low acid experiments by a series of pre-equilibrations with a large excess of 1.000 *M* sodium perchlorate plus 1.000 *M* perchloric acid. The resin then was washed and dried as above.

Perchloric acid stock solutions were prepared by dilution of the G. F. Smith double vacuum distilled product and titration with standard base. Stock solutions of sodium perchlorate were prepared by neutralizing primary standard grade sodium carbonate with perchloric acid; the solutions were analyzed by gently evaporating aliquots to dryness, drying the residue for several hours at 160° and weighing as $NaClO_4$. All other reagents were of C.P. grade and were used without additional purification. Triply distilled water was used to prepare all solutions.

Results and Discussion

Cation-exchange Studies.—The necessary equations and conditions for the derivation of complexing constants from exchanger data have been presented by Fronaeus[3] and need not be repeated here. Only minor modifications will be applied to Fronaeus's notation. The experimental results are presented in the form of the phase distribution function $\phi = C_{MR}/C_M$ where C_{MR} is the equilibrium total concentration of metal ion in the resin phase and C_M the corresponding total metal ion concentration in solution.

The resin load C_{MR} is evaluated from the equation

$$C_{MR} = (v/m)(C_M' - C_M\delta) \qquad (1)$$

where v equals the volume of solution added to m grams of resin. Primes applied to any symbol indicate a concentration (or counting rate) before the addition of resin. The resin swelling factor is represented by δ; and at the 83 ml./g. value of v/m used in this research, δ values of 0.996 and 0.995 were found, respectively, for the hydrogen ion form and mixed sodium–hydrogen ion form of the resin. These quantities were determined by the increase in hydrogen ion concentration of appropriate perchloric acid solutions after contact with the dried resin.

Since all thorium concentrations were assayed at constant geometry on a fixed sample, ϕ is calculated from the experimental data by

$$\phi = (v/m)(R' - R\delta)/R \qquad (2)$$

where R represents the counting rate of the sample. The concentration of free ligand (considered here as $HSO_4^- + SO_4^{-2}$) and the total ligand concentration are represented as [A] and C_A. Since in all runs $C_M << C_A$, [A] was evaluated readily by the relationship $[A] = C'_A/\delta$.

It has been well demonstrated that the magnitude of ϕ is dependent on the resin load, decreasing as C_{MR} increases.[3,9] For this reason any series of ϕ values employed to calculate complexing constants must correspond to a reasonably constant value of C_{MR}. Generally this is accomplished by determining ϕ as a function of C_M for each C_A followed by graphical interpolation to a fixed nominal value of C_{MR}. However, in this research the high affinity of thorium for the resin rendered this procedure unnecessary except at the four highest ligand concentrations in the low acid series. The percentage correction to all other ϕ values is estimated to be less than the experimental error.

The ion exchanger data and the calculated quantities ϕ and C_{MR} are presented in Table I Values of C_{MR} were obtained from the relation $C_{MR} = C_M'\phi R/R'$. Sufficiently accurate estimates of C_M' for this purpose could be made on the basis of the known initial amount of carrier thorium and the measured yields for each tracer preparation. Additional known amounts of thorium were added in the experiments designed to determine the dependence of ϕ on C_{MR}. The tabulated counting rates include any dilution factors used in obtaining samples. Each R' value represents the mean of four independent measurements.

Since this research deals with the protonated ligand HSO_4^-, it is necessary to modify Fronaeus's[3] general treatment to include the hydrogen ion dependence of the complexing reactions. Representing the concentration of free bisulfate ion by $[HA^-]$ and defining for brevity the quantity $A^* = [HA^-]/[H^+]$, it is readily shown that

$$A^* = [A]/([H^+] + K_d) \qquad (3)$$

where K_d is the dissociation constant for bisulfate and has a reported value[2c] of 0.084 mole/l. at 25° and an ionic strength of two. Anticipating our observed hydrogen ion dependence, the cumulative association constants β_j refer to the complexing reactions written in the general form

$$Th^{+4} + {}_jHA^- = ThA_j^{+4-2j} + {}_jH^+ \qquad (4)$$

Use of the terms A^* and β_j as defined above allows a derivation of the necessary equations in the identical form presented by Fronaeus.[3] Assuming that only the species Th^{+4} and $ThSO_4^{+2}$ are sorbed by the resin, the function $1/\phi$ can be expressed as

$$\frac{1}{\phi} = \frac{(1/l_0)(1 + \beta_1A^* + \ldots \beta_NA^{*N})}{1 + lA^*} \qquad (5)$$

where $l = l_1\beta_1/l_0$ and l_0 and l_1 are the respective distribution coefficients of Th^{+4} and $ThSO_4^{+2}$ between the resin and solution phase. Under the conditions listed by Fronaeus,[3] these distribution coefficients are assumed to be constants.

The presence of the l parameter in equation 5 renders the solution for the various β_j values an awkward problem. The procedure devised by Fronaeus[3] requires the graphical extrapolation of ϕ and two successively derived functions to zero ligand concentration. Since all three functions are non-linear and the accuracy of the derived functions depends on the success of the preceding extrapolation, the accumulative error in the final results could be excessively large. However, it is possible to obtain the best values of the parameters

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[9] (a) B. G. F. Carleson and H. Irving, *J. Chem. Soc.*, 4390 (1954); (b) N. Sunden, *Svensk Kem. Tidskr.*, **66**, 173 (1954).

TABLE I

A. CATION-EXCHANGE DATA IN 2 M H^+ AT 25°

$A = HSO_4^- + SO_4^{-2}$; $R' = 4.01 \times 10^5$ c./min.

$[A] \times 10^3$, moles/l.	v/m, ml./g.	$R \times 10^{-3}$, c./min.	$C_{MR} \times 10^7$, moles/g.	ϕ, l./g.
0	82.7	0.172	6.0	193
0	82.1	.176	6.0	187
1.065	82.3	.186	6.0	177
2.140	82.3	.199	6.0	166
4.28	82.7	.236	6.0	140
6.42	82.5	.251	6.0	132
8.56	82.8	.284	6.0	117
10.69	82.3	.344	6.0	95.7
20.37	82.7	.507	6.0	65.3
40.8	82.1	.964	6.0	34.1
50.9	82.3	1.258	6.0	26.2
61.1	82.4	1.507	6.0	21.9
71.2	82.1	1.890	6.0	17.4
81.6	82.4	2.16	6.0	15.2
91.6	82.4	2.42	6.0	13.6
101.8	82.8	2.87	6.0	11.5
152.8	82.5	5.53	5.9	5.90
203.6	82.4	8.93	5.9	3.62

B. CATION-EXCHANGE DATA IN 1 M H^+ + 1 M Na^+ AT 25°

$A = HSO_4^- + SO_4^{-2}$; $R' = 4.87 \times 10^5$ c./min.

$[A] \times 10^3$, moles/l.	v/m, ml./g.	$R \times 10^{-3}$, c./min.		$C_{MR} \times 10^7$, moles/g.	ϕ, l./g.	
0	81.7	1.577		9.2	25.2	
0	82.3	1.538		9.2	26.0	
0.976	81.3	1.821		9.1	21.7	
1.961	82.0	1.937		9.2	20.5	
2.933	81.7	2.32		9.1	17.0	
3.93	81.7	2.58		9.1	15.3	
4.90	82.1	2.90		9.2	13.7	
6.86	81.7	3.34		9.1	11.85	
8.82	81.6	3.93		9.1	10.05	
11.77	81.8	5.01		9.1	7.88	
14.72	82.2	6.22		9.1	6.36	
20.13	82.2	8.29		9.1	4.75	
30.11	82.2	12.45		9.0	3.14	
40.3	81.8	18.10		8.8	2.12	
60.3	82.0	31.6		8.6	1.18	
80.5	82.1	46.8		8.3	0.774	
100.6	82.2	63.4		8.0	.549	
100.6	83.7	2.38		10.9	.534	
100.6	83.0	2.44	a	14.3	.514	c1
100.6	83.2	2.43		17.9	.518	
120.8	81.9	85.1		7.6	.387	
120.8	83.0	3.12		10.2	.384	
120.8	83.6	3.24	a	13.6	.370	c2
120.8	83.7	3.28		17.0	.365	
151.0	81.9	110.2		7.1	.281	
151.0	84.0	4.43	a	15.7	.249	c3
201.2	82.8	8.10		2.8	.183	
201.2	83.0	8.25	b	5.7	.179	c4
201.2	82.5	8.60		8.3	.167	
201.2	82.9	8.90		10.9	.160	

[a] $R' = 1.775 \times 10^4$ c./min. [b] $R' = 2.60 \times 10^4$ c./min. [c] Interpolating to $C_{MR} = 9.1 \times 10^{-7}$ mole/g.: ϕ = [1]0.540, [2]0.385, [3]0.273 and [4]0.165 l./g.

and, of great importance, their statistical standard deviations by the rigorously objective treatment of weighted least squares. The eminent desirability of such analysis and its greatly enhanced feasibility through the use of high speed computers is pointed out by Rydberg and Sullivan.[10]

Application of least squares to equation 5 is merely a particular case in the general treatment of formulas that are non-linear in the unknown constants. Solution of the problem requires that estimates be made in any convenient way of each of the parameters, and the least squares technique is then employed to calculate corrections to these estimated values.[11] Preliminary application of Fronaeus's[3] graphical treatment had indicated that only the first two sulfate complexes need be considered and that the value of l in relation to β_1 was too small to be detected.[12] Accordingly the first estimate of the parameters was obtained by setting l equal to zero and running a conventional weighted least squares on $1/\phi$ as a quadratic in A^* to obtain estimated values of l_0, β_1 and β_2. The weighting procedure was based on the assumption that the counting rate R contributed the dominating error to ϕ, and the errors in R were calculated from the total number of counts observed for each sample. The weight w of each $1/\phi$ then is given by

$$w = k\phi^2(R' - R\delta)^2/(\alpha R')^2 \qquad (6)$$

where k is a proportionality constant and α is the percentage error of R. The final least squares corrected values and standard deviations obtained for l were -1.3 ± 1.4 and -0.04 ± 0.41 for the 2 and 1 M acid data, respectively. The physically impossible negative values and standard deviations in excess of 100% indicate, within the accuracy of the data, the l parameter has a negligible effect on $1/\phi$ and can be set equal to zero.

The magnitude of l was expected to be fairly small but finding it negligibly so was a surprising result. Therefore experimental evidence in support of this claim was sought by measuring the distribution coefficient of uranyl ion between the resin and 2 M perchloric acid. This was based on the assumption that the sorption of UO_2^{+2} would provide at least a rough measure of l_1 for $ThSO_4^{+2}$. Using the alpha tracer U-233 at a resin load C_{MR} of 1.1×10^{-6} mole/g., the mean and standard deviation of four determinations at 25° was $C_{MR}/C_M = (4.46 \pm 0.04) \times 10^{-2}$ l./g. Combining this result with the β_1 and 2 M acid value of l_0 tabulated below, the estimated value of l is 0.038. Since the highest value of A^* employed was about 0.2, the maximum error in $1/\phi$ produced by the neglect of the lA^* term is thus estimated at somewhat less than 1%. Even a tenfold increase in this estimated value would amply confirm the least squares result that the effect of l on $1/\phi$ is too small to be detected.

With l assumed negligibly small the final least squares values of the remaining parameters correspond directly to the preliminary estimates. The degree of fit to all the data achieved with these values is illustrated in Fig. 1. A linear plot is obtained by use of the function ϕ_1 defined as

$$\phi_1 = (l_0\phi^{-1} - 1)/A^* \qquad (7)$$

With l zero and only the first two complexes

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[10] J. Rydberg and J. C. Sullivan, *Acta Chem. Scand.*, in press.

[11] Details of the method are presented in numerous texts. See for example: J. B. Scarborough, "Numerical Mathematical Analysis," 2nd Ed., The John Hopkins Press, Baltimore, 1950, p. 463.

[12] Graphical analysis of the 1 M acid data gave the results: l_0 = 25.6 l./g., $\beta_1 - l$ = 166, β_1 = 165 and $\beta_2 = 3.7 \times 10^3$, all in remarkable agreement with the final least squares values. The larger scatter of the 2 M acid data made the graphical treatment too uncertain for a satisfactory objective analysis.

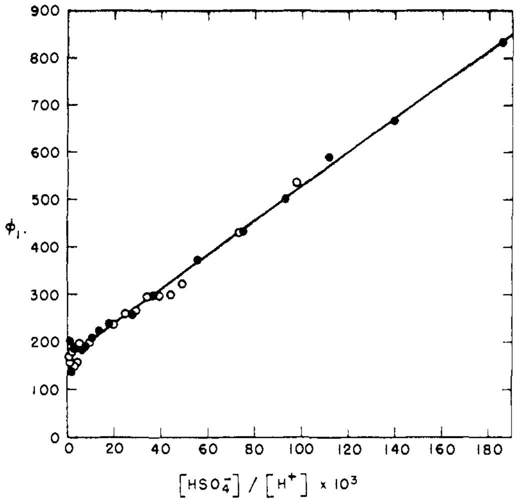

Fig. 1.—Graphic presentation of the thorium sulfate complexing data. Intercept = β_1 and slope = β_2. Open circles, 2 *M* H$^+$; closed circles, 1 *M* H$^+$ + 1 *M* Na$^+$.

present, it follows readily that $\phi_1 = \beta_1 + \beta_2 A^*$. A summary of the weighted least squares results[13] is listed in Table II with all ± values indicating the statistical 95% confidence limits. The final weighted mean values of β_1 and β_2 correspond to the intercept and slope of the straight line in Fig. 1. The l_0 values are for two markedly different resin preparations and would not be expected to agree.

TABLE II

SUMMARY OF LEAST SQUARES ANALYSIS OF EXCHANGER DATA; μ = 2.00, t = 25°

$[H^+]$	l_0(l./g.)	β_1	$\beta_2 \times 10^{-3}$
2 *M*	192 ± 11	164 ± 18	3.49 ± 0.44
1 *M*	25.6 ± 0.7	167 ± 9	3.63 ± 0.21
	Weighted mean	166 ± 8	3.61 ± 0.19

The results of this research are in good agreement with the TTA extraction study of Zebroski, Alter and Heumann.[2c] At 25° and in similar medium they found two complexes with the association constants β_1 = 159 and $\beta_2 \times 10^{-3}$ = 2.85 + 0.8 [H$^+$]. The trend of their β_2 value with hydrogen ion was interpreted as indicating part of the second complex to be in the form $ThHSO_4SO_4^+$; however, no evidence for such a species is found in this investigation.

Calorimetry.—Interpretation of the calorimetric data is based on the simultaneous heat effects of the three reactions

$$Th^{+4} + HSO_4^- = ThSO_4^{+2} + H^+ \quad (8)$$

$$Th^{+4} + 2HSO_4^- = Th(SO_4)_2 + 2H^+ \quad (9)$$

$$SO_4^{-2} + H^+ = HSO_4^- \quad (10)$$

with rapid attainment of equilibrium assumed for all the reactions.[14] The correct apportionment of the gross heat change is dependent on the accuracy of the individual equilibrium constants; hence, the data are presented in sufficient detail to allow a complete recalculation of the results.

The direct measurement of ΔH_{10} by independent experiments provides a simplification in the heats of complexing calculations and also partially cancels errors due to the bisulfate dissociation constant K_d. Accordingly the heat of reaction 10 was measured by addition of approximately 5 ml. of a 0.4 *M* sodium sulfate plus 1.2 *M* sodium perchlorate stock solution to 195 ml. of 0.2 *M* perchloric acid plus 1.8 *M* sodium perchlorate. A "blank" or correction due to the combined heat of breaking the bulb and heat of mixing the reactant solutions was obtained by addition of a like amount of the sample bulb stock solution to 2 *M* sodium perchlorate.[15] The mean and standard deviation of three such "blank" determinations was −0.226 ± 0.019 cal. evolved.

A summary of the data and results is presented in Table III. The amount of bisulfate formed in each run was obtained using K_d = 0.084.[2c] The listed ± value on the final result is based on an estimated 10% uncertainty in K_d, which under the concentration conditions of these experiments will produce a 3% error in the calculated ΔH_{10}. The results may be compared with the 25° standard state value 5.2 ± 0.5 kcal. determined calorimetrically by Pitzer[16] and the recent result 5.6 ± 0.2 kcal. obtained from temperature coefficient of e.m.f. data by Nair and Nancollas.[17]

TABLE III

HEAT OF ASSOCIATION OF HSO_4^- IN IONIC STRENGTH 2.00 AT 25°

B_f × 10^3, moles	C_f × 10^3, moles	D_f × 10^3, moles	V_f, ml.	Q_c, cal.	ΔH_{10}, kcal.
40.18	356.9	2.011	200.2	−7.773	5.542
40.24	356.1	2.007	200.3	−7.737	5.526
40.06	356.9	2.010	200.2	−7.763	5.542
				Mean value	5.54 ± 0.17

To facilitate presentation of the calorimetric data in Tables III and IV, the following terms are defined: Q = observed heat evolved; $Q_c = Q$ − "blank" correction; V = volume; A, B, C, D and E = moles of H_2SO_4, $HClO_4$, $NaClO_4$, Na_2SO_4 and $Th(ClO_4)_4$, respectively. The subscripts b, d and f indicate the bulb solution, Dewar solution before breaking the sample bulb and the final solution.

The heats of sulfate complexing were carried out by addition of approximately 5 ml. of a 0.4 *M* thorium perchlorate in 0.4 *M* perchloric acid stock solution (except for the first two runs where a more concentrated form of the same solution was used) to 195 ml. of a perchloric acid–sulfuric acid solution of varying composition totaling to 2 *M*. The "blank" was obtained by adding the same thorium

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(13) A complete calculation was also made assuming 3 complexes; and although small positive values were obtained for β_3, standard deviations in excess of 100% indicated the results to be without significance.

(14) This was indicated to be the case by the observed linear drift rates of the thermocouple potential after breaking the sample bulb (first reading usually 1.5 min. after breaking bulb).

(15) Since the heat of reaction and heat of mixing or dilution cannot be separated, only approximations can be made to the true "blank" correction. By matching the sodium ion concentration of both reactant solutions, the "blank" correction was made fairly small. It is then assumed that replacing 10% of the sodium with hydrogen ion will not introduce a serious error. Similarly in the heats of complexing experiments the perchlorate concentration of both solutions was matched, and a portion of the ClO_4^- is replaced by HSO_4^- in the main experiments.

(16) K. S. Pitzer, THIS JOURNAL, **59**, 2365 (1937).

(17) V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 4144 (1958).

TABLE IV

HEATS OF THORIUM SULFATE COMPLEXING AT IONIC STRENGTH 2.00 AND 25°

$A_d \times 10^3$, moles	$B_d \times 10^3$, moles	$B_b \times 10^3$, moles	$E_b \times 10^3$, moles	V_b, ml.	V_f, ml.	Q_c, cal.	$A^* \times 10^3$	X	Y, kcal./mole
2.205	387.7	1.858	2.041	2.283	199.7	0.305[a1]	3.382	0.074	0.684
6.588	383.3	1.829	2.010	2.247	200.4	.608[a2]	11.85	.258	.875
6.302	382.9	1.820	2.000	5.108	199.7	.694	11.29	.246	.935
10.62	378.7	1.828	2.008	5.129	199.9	.926	20.55	.447	1.199
14.97	375.3	1.825	2.005	5.121	200.0	1.059	30.28	.658	1.459
19.22	371.4	1.827	2.007	5.128	200.0	1.192	40.00	.870	1.756
23.72	366.5	1.824	2.004	5.120	200.0	1.305	50.49	1.098	2.084
28.46	361.2	1.827	2.008	5.128	200.2	1.460	61.68	1.341	2.503
32.15	358.6	1.823	2.002	5.115	200.0	1.508	70.20	1.527	2.755
36.60	355.5	1.825	2.005	5.121	200.9	1.542	80.41	1.749	3.035
40.66	350.7	1.820	1.999	5.107	200.3	1.597	90.20	1.962	3.349

[a] "Blank" correction = [1]3.600 and [2]3.545 cal. evolved.

stock solution to 2 M perchloric acid[15]; three determinations gave a mean and standard deviation of −0.083 ± 0.031 cal. evolved. The corrected heat evolved is apportioned among reactions 8, 9 and 10 by

$$Q_c = -[\mathrm{ThSO_4}^{+2}]V_f\Delta H_8 - [\mathrm{Th(SO_4)_2}]V_f\Delta H_9 - \{[\mathrm{SO_4}^{-2}]_d V_d - [\mathrm{SO_4}^{-2}]_f V_f\}\Delta H_{10} \quad (11)$$

with the bracketed quantities indicating concentrations in moles/l. Defining the quantity Y by

$$Y = Q_c + \{[\mathrm{SO_4}^{-2}]_d V_d - [\mathrm{SO_4}^{-2}]_f V_f\}\Delta H_{10}/[\mathrm{ThSO_4}^{+2}]V_f \quad (12)$$

and letting $X = [\mathrm{Th(SO_4)_2}]/[\mathrm{ThSO_4}^{+2}]$, substitution into (11) gives the linear equation

$$Y = -\Delta H_8 - \Delta H_9 X \quad (13)$$

Simultaneous solution of equations based on the known initial concentrations and the equilibrium constants β_1, β_2 and K_d yielded the quantity $A^* = [\mathrm{HSO_4}^-]/[\mathrm{H}^+]$, from which the equilibrium concentration of all species can be readily calculated.

A summary of the data and calculations is presented in Table IV. A plot of the observed Y *vs.* X values and the calculated weighted least squares straight line is illustrated in Fig. 2. With equal weight assigned to the corrected heat of each calorimetric run,[18] the weight of each Y is proportional to $V_f^2[\mathrm{ThSO_4}^{+2}]^2$.

The standard deviations calculated for ΔH_8 and ΔH_9 on the basis of the least squares analysis reflect the uncertainties due to the random error in Q_c, but it is also necessary to consider the possible fixed errors engendered by uncertainties in the constants β_1, β_2 and K_d. Using β_1 as an example, this was done by evaluation of $\partial X/\partial\beta_1$ and $\partial Y/\partial\beta_1$ for each experimental point. The product of the respective partial derivatives and assumed uncertainty in β_1 then furnished, in effect, a complete recalculation of each X and Y for β_1 at either extreme of its estimated ± range. By repeating the least squares analysis on these new values of X and Y, the corresponding range of ΔH_8 and ΔH_9 was obtained. A surprising result of this analysis is that the ΔH values are relatively insensitive to errors in both β_1 and β_2. This is not true of the individual X and Y values; however, the resulting points are shifted approximately along the straight line of Fig. 2 with consequently little change in the slope and intercept. Indicating the various errors by σ, a summary of the error analysis is listed in Table V. All σ values correspond to the 95% confidence level with the exception of that due to K_d where again a 10% uncertainty was assumed.

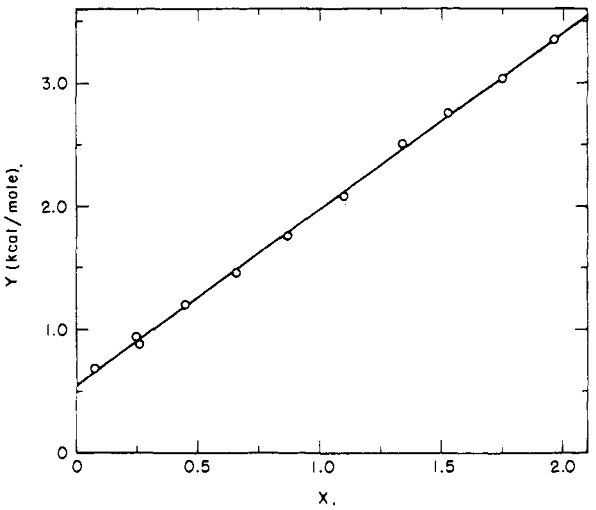

Fig. 2.—Graphic presentation of the heats of thorium sulfate complexing. Intercept = $-\Delta H_8$ and slope = $-\Delta H_9$.

TABLE V

SUMMARY OF ERROR ANALYSIS OF THE HEATS OF COMPLEXING

Error due to	σ of ΔH_8, kcal.	σ of ΔH_9, kcal.
σ of Q_c (0.071)	0.040	0.042
σ of β_1 (±8)	± .002	∓ .014
σ of β_2 (±190)	± .006	± .011
σ of K_d (±10%)	∓ .031	∓ .046
$(\Sigma\sigma^2)^{1/2}$	.051	.065

TABLE VI

SUMMARY OF THERMODYNAMIC QUANTITIES AT IONIC STRENGTH 2.00 AND 25°

Reaction	K	ΔF, kcal.	ΔH, kcal.	ΔS, e.u.
8	166 ± 8	−3.03 ± 0.03	−0.54 ± 0.05	8.4 ± 0.2
14	21.7 ± 1.5	−1.83 ± .04	−0.89 ± .08	3.2 ± .3
10	11.9 ± 10%[a]	−1.47 ± .06	5.54 ± .17	23.5 ± .6

[a] Units = l./mole.

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(18) It is interesting to note that the least squares analysis indicated the standard deviation of Q_c to be 0.031 cal., which corresponds exactly to the uncertainty listed for the "blank" correction.

A final summary of the thermodynamic quantities for the sulfate complexes of thorium and the association of bisulfate ion is presented in Table VI. The values for the second complex correspond to the more conventional stepwise form of the reaction

$$\mathrm{ThSO_4^{+2} + HSO_4^- = Th(SO_4)_2 + H^+} \quad (14)$$

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Lemont, Illinois

[Contribution from the Thermal Laboratory, The Dow Chemical Company]

The Chemical Thermodynamic Properties of Calcium Hydroxide

By W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull

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The heat capacity of crystalline calcium hydroxide was measured from 19 to 330°K. and the entropy at 298.15°K. calculated as 19.93 ± 0.10 cal. deg.$^{-1}$ mole^{-1}. The heat of dissociation was calculated from dissociation pressures by third law methods. The result is in excellent agreement with calorimetric values, indicating no residual entropy at 0°K. Selected best values for the heat and free energy of formation at 298.15°K. are −235.71 and −214.77 ± 0.10 kcal. mole^{-1}, respectively.

Introduction

Although an accurate value is available for the heat of dissociation of calcium hydroxide,[1] the entropy listed by Kelley[2] is based on fragmentary data. The free energy of formation calculated from dissociation pressures indicates Kelley's value to be too low. The entropy of calcium hydroxide therefore was determined by measurement of the heat capacity from 19 to 330°K.

Experimental

Calcium hydroxide was prepared by calcining Mallinckrodt Analytical Reagent calcium carbonate and treating the resulting oxide with a stoichiometric amount of water. Analysis indicated the sample to be 99.75% calcium hydroxide with the remainder calcium carbonate and water. The purity was considered adequate for heat capacity purposes. An X-ray diffraction pattern indicated the sample to be crystalline.

Heat capacity measurements were made over the range 19 to 330°K. with an automatically operated adiabatic calorimeter that has been described previously.[3,4] A sample weighing 39.010 g. corrected to vacuum, was sealed in a nickel-plated copper calorimeter under one atmosphere pressure of helium gas at room temperature. The filling and sealing operation were done under anhydrous, CO_2-free conditions so as to avoid contamination of the sample. The experimental heat capacity data are given in Table I. Temperatures and temperature differences were measured with a platinum resistance thermometer (R_0 = 96 ohms) calibrated by comparison with an N.B.S. calibrated platinum thermometer. Temperature rises were approximately 10% of the absolute temperature below 50°K. and 5 to 7% at higher temperatures. Corrections for curvature were not applied, nor should they be necessary with intervals of this size. The heat capacities are believed to be accurate to within 0.2 to 0.3% above 50°K. and to within 1% at lower temperatures. The accuracy estimates are based on the results of a series of check measurements on a heat capacity standard, as well as on the results of several inter-laboratory comparisons. Results are given in terms of the defined thermochemical calorie, equal to 4.1840 abs. joules. The ice point was taken as 273.15°K. and the molecular weight of calcium hydroxide as 74.096.

Table I

The Heat Capacity of Calcium Hydroxide, Cal. Mole^{-1} Deg.$^{-1}$

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		159.46	13.63	136.07	11.60
18.85	0.177	170.25	14.35	140.62	12.02
21.27	.268	175.35	14.83	145.06	12.50
23.76	.352	181.34	15.17	150.42	12.74
26.49	.505	188.21	15.64	156.65	13.39
29.81	.671	194.92	16.08	162.67	13.83
33.26	.887	201.50	16.47	168.52	14.29
36.90	1.185	207.98	16.86	174.24	14.68
41.26	1.466	214.36	17.17	179.86	15.17
45.79	1.867			185.38	15.48
50.04	2.211	Series II		190.82	15.84
54.28	2.677	22.91	0.312	196.84	16.21
59.05	3.158	25.92	.448	203.44	16.54
63.93	3.677	28.95	.608	209.94	17.00
68.30	4.257	32.02	.862	216.35	17.33
71.72	4.477	35.24	1.029	222.68	17.68
76.89	5.040	38.77	1.310	228.92	18.08
83.03	5.814	42.84	1.577	247.18	18.85
88.65	6.492	47.54	1.944	253.17	19.15
93.92	6.975	52.61	2.378	259.09	19.41
98.89	7.778	57.84	2.952	264.96	19.63
103.61	8.205	63.33	3.623	270.78	19.88
108.15	8.699	69.12	4.263	276.55	20.07
112.52	9.171	75.18	4.856	282.28	20.31
116.75	9.587	81.01	5.590	287.96	20.54
120.86	10.03	87.22	6.322	294.16	20.75
124.85	10.40	105.78	8.440	300.86	21.06
130.01	10.93	111.30	9.108	307.87	21.35
136.27	11.62	116.59	9.630	315.18	21.61
142.33	12.09	121.69	10.13	322.43	21.80
148.22	12.62	126.62	10.67	329.62	22.10
153.93	13.16	131.41	11.11		

The entropy, free energy and heat content functions of crystalline calcium hydroxide, obtained by graphical integration of the heat capacity data, are listed at even tempera-

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