TABLE I

VALUES OF THE DETERMINANT FOR VARIOUS CONSTANTS REPORTED FOR URANIUM SULFATE COMPLEXES

$(HSO_4^-) \times 10^3$ \ β_1, β_2	131^a 1380	131^a 1320	128^a 1370	130^a 1330	128^b 1480	126^c 1210	126^c 1160	168^d 62.2
1.83	+0.0073	+0.0074	+0.0108	+0.0085	+0.0107	+0.0135	+0.0136	−0.0311
4.59	− .0585	− .0577	− .0474	− .0541	− .0489	− .0364	− .0371	− .2306
9.18	− .0144	− .0117	+ .0066	− .0053	+ .0017	+ .0298	+ .0370	− .2205
18.35	− .0570	− .0400	− .0087	− .0277	− .0394	+ .0670	+ .0811	− .2273
45.9	+ .4119	+ .5107	+ .5555	+ .5366	+ .3745	+ .9037	+ .9859	+1.0329
45.9	− .3018	− .1892	− .1509	− .1639	− .3572	+ .2376	+ .3314	+0.5502
92.5	− .3979	+ .0685	− .0491	+ .0813	−1.0332	+1.3751	+1.7637	+6.5200

Methods employed: [a] Leden, [b] Bjerrum, [c] Fronaeus, [d] Betts and Leigh.

$$\begin{vmatrix} \frac{(M) - C_M}{(M)} & \frac{\beta_1\gamma_M\gamma_a}{\gamma_1} & \cdots & \frac{\beta_n\gamma_M\gamma_a{}^n}{\gamma_n} & 0 & \cdots\cdots & \\ -\frac{C_A}{(M)} & \frac{1}{(M)} + \frac{\beta_1\gamma_M\gamma_a}{\gamma_1} & \cdots & \frac{n\beta_n\gamma_M\gamma_a{}^n}{\gamma_n} & 0 & \cdots\cdots & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \\ 0 & 0 & \cdots & \frac{(M) - C_M}{(M)} & \frac{\beta_1\gamma_M\gamma_a}{\gamma_1} & \cdots & \frac{\beta_n\gamma_M\gamma_a{}^n}{\gamma_n} \\ 0 & 0 & \cdots & -\frac{C_A}{(M)} & \frac{1}{(M)} + \frac{\beta_1\gamma_M\gamma_a}{\gamma_1} & \cdots & \frac{n\beta_n\gamma_M\gamma_a{}^n}{\gamma_n} \end{vmatrix} = 0$$

Now if the values for the constants, the activity coefficient and the experimental quantities are put into the determinant for each experimental point, the values for the determinant should, in the ideal case, all be zero. Since, however, experimental errors are present always, the criterion of validity of the constants is the oscillation of the sign of the expanded determinant as the experimental conditions are changed.

As an example we shall investigate the validity of the constants for uranium sulfate complexes obtained by Sullivan and Hindman[2] from the data of Betts and Leigh.[4] Since the activity coefficients are not known and were not used in the calculation of the constants, the values are for concentration constants and the activity coefficients are included in the calculated association constants. In order to make the terms in the expanded determinant have the same order of magnitude for the various experimental points, we multiply the determinant by $(M)^2$. For the case of Betts and Leigh's data with only two constants, the determinant then becomes

$$(M)^2 \begin{vmatrix} \frac{(M) - C_M}{(M)} & \beta_1 & \beta_2 & 0 \\ -\frac{C_A}{(M)} & \frac{1}{(M)} + \beta_1 & 2\beta_2 & 0 \\ 0 & \frac{(M) - C_M}{(M)} & \beta_1 & \beta_2 \\ 0 & -\frac{C_A}{(M)} & \frac{1}{(M)} + \beta_1 & 2\beta_2 \end{vmatrix}$$

Table I lists the values of the determinant obtained using the various values of constants calculated for Betts and Leigh's data as reported by Sullivan and Hindman.[2] It is evident that the values $\beta_1 = 128$ and $\beta_2 = 1370$ give the best fit of those listed. It is also apparent that the constants as obtained by Betts and Leigh's and Fronaeus' procedures do not fit the data. The experimental points represented by row 2 and row 5 must have relatively large experimental errors because in the first case the determinant is always negative and in the second case it is always positive.

The method developed is also applicable to polynuclear species except that the coefficients of the power series will contain (M) explicitly in all coefficients corresponding to complex species which contain more than one M. In principle it would be possible to obtain the constants by a least-squares treatment of the expanded determinant using all of the data at once with the elimination of approximation and graphical methods. This would be a reasonable approach for the uranium sulfate complexes but for cases involving more than two or three constants the method becomes much too tedious, and therefore its most useful feature is in testing the validity of constants derived by other procedures.

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[4] R. H. Betts and R. Leigh, *Can. J. Research*, **B28**, 374 (1949).

The Heat of Solution of Sodium Borohydride and the Entropy of Borohydride Ion[1]

BY STUART R. GUNN AND LEROY G. GREEN

RECEIVED JULY 27, 1955

The heat of formation of crystalline sodium borohydride has been determined by Davis, Mason and Stegeman,[2] and the free energy of aqueous borohydride ion has recently been measured by Stockmayer, Rice and Stephenson.[3] In the present work the heat of solution of sodium borohydride has been measured and the heat of formation and entropy of the ion have been derived.

Experimental

Sodium borohydride (Metal Hydrides, Inc., Beverly, Mass.) was purified by two successive recrystallizations from M2M (diethylene glycol dimethyl ether), the solution being saturated at 40° and heated to 100° in order to precipitate the unsolvated crystals.[4] All operations were performed in a closed system or under an argon atmosphere. The material was filtered and dried under vacuum for three days at 80–90°. The product was analyzed gasometrically

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] W. D. Davis, L. S. Mason and G. Stegeman, THIS JOURNAL, **71**, 2775 (1949).

[3] W. H. Stockmayer, D. W. Rice and C. C. Stephenson, *ibid.*, **77**, 1980 (1955).

[4] H. C. Brown, "The Chemistry of Trialkoxyborohydrides," American Chemical Society, Cincinnati, 1955.

by hydrolysis with HCl; three determinations gave values of 99.0, 99.6 and 99.8% of theoretical hydrogen.

The calorimeter used was a new instrument to be described more fully at a later date. It consists of a copper bomb of 700-ml. volume suspended in an evacuated submarine. Stirring is accomplished by rocking the assembly continually through 180°, and the reaction is initiated by rotating it an additional 90° to unbalance a spring-loaded hammer which breaks the sample-bulb. Temperature changes are measured with a G-2 Mueller bridge and a calorimetric resistance thermometer to a precision of 0.0001°. Calibration is performed electrically, using a constantan heater, a regulated voltage power supply, a Rubicon Type B precision potentiometer, calibrated standard resistors and a relay operated from a standard clock.

The bomb was loaded with 400 ml. of water and 5.00 ml. of 1.000 N NaOH to retard hydrolysis of the borohydride. In the third and fourth runs, the solution was degassed by repeated stirring and pumping through a vacuum line. Reactions were initiated at 25.00 ± 0.03°. Dissolution occurred very rapidly; the temperature change with the samples used was from 0.07 to 0.09°. The calorimeter was then cooled and calibrated electrically over approximately the same range.

Results

Four runs were performed as listed in Table I.

TABLE I

HEAT OF SOLUTION OF $NaBH_4$

Run	N, $\frac{\text{moles H}_2\text{O}}{\text{moles NaBH}_4}$	$-\Delta H$, $\frac{\text{cal.}}{\text{mole}}$
1	378	714
2	349	717
3	360	709
4	311	706

Since it is possible that there might be some reaction of borohydride with dissolved oxygen, the last two runs will be weighted more heavily and we will write for the reaction

$$NaBH_4(c) + 350H_2O(e) = NaBH_4 \cdot 350H_2O \quad (1)$$
$$\Delta H = -709 \pm 5 \text{ cal.}$$

The most probable systematic error would be due to the presence of a sodium borate; 0.5 weight % $Na_2B_4O_7 \cdot 5H_2O$ would make the above value 10 cal. too positive. To correct to infinite dilution, we shall assume that the heat of dilution is the same as that for NaBr given by Harned and Owen[5] and shall ignore the effect of the 0.0124 M NaOH in the solutions. Hence for the reaction

$$NaBH_4(c) = Na^+ + BH_4^- \quad (2)$$
$$\Delta H^\circ_{298} = -776 \text{ cal.}$$

Since the heats of dilution of NaBr and NaI differ by only 10 or 20 cal. over this range,[6] it seems probable that this value is reliable within these limits.

Applying a correction for the present best value for the heat of formation of $H_3BO_3 \cdot \infty H_2O$, −257.32 kcal.,[7] the value of Davis, Mason and Stegeman[2] for the heat of formation of $NaBH_4(c)$ becomes −46.15 kcal. Using −57.279 kcal. for the heat of formation of Na^+,[6] the standard heat of formation of borohydride ion is calculated to be +10.4 kcal., the largest uncertainty being in the heat of formation of boric oxide.

For the reaction 2, Stockmayer, Rice and Stephenson give the value $\Delta F^\circ_{298} = -5660 \pm 70$ cal. From this and the ΔH°_{298}, one obtains $\Delta S^\circ_{298} = +16.4 \pm 0.3$ e.u. Using the standard entropies of 24.26 for $NaBH_4(c)$[8] and 14.4 for Na^+,[6] the entropy of borohydride ion is found to be 26.3 e.u., in good agreement with the value of 25.5 ± 1 estimated by various means.[3]

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[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950.

[6] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Circular of the NBS, No. 500, 1952.

[7] E. J. Prosen, "Thermochemistry of Boron Hydrides and Related Compounds," American Chemical Society, Cincinnati, 1955.

[8] H. L. Johnston and N. C. Hallett, THIS JOURNAL, **75**, 1467 (1953).

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On the Rate of the *cis–trans* Interconversion of Dichlorobis-(ethylenediamine)-cobalt(III) Chloride

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The *cis–trans* interconversion between the praseo and violeo complex was discovered by Jorgensen.[1] This note is concerned with the evaluation of certain kinetic data for the *cis–trans* interconversion of $[Co(en)_2Cl_2]Cl$.[2]

trans-$[Co(en)_2Cl_2]Cl$ was prepared as described by Bailar.[3] The green *trans* form is spontaneously converted into a violet *cis* form on standing in aqueous solution. The rate of conversion was followed with a Beckman D.U. spectrophotometer using 1.00% by weight (0.035 M) solutions of the *trans* form in all cases. It was found from a study of the spectrum of the *cis* and *trans* forms that a wave length of 6000 Å. was suitable for following the rate of reaction. The temperature was controlled to ±0.2°.

The rate constants were calculated from the equation

$$k = \frac{2.303}{t} \log \frac{T_\infty - T_0}{T_\infty - T_t}$$

where

k = rate constant
T_∞ = transmittance at infinite time
T_0 = transmittance at zero time
T_t = transmittance at time t
t = time in seconds

The rate constants at various temperatures are listed in Table I.

TABLE I

Temp., °C.	k(sec.$^{-1}$)
26.0	2.50×10^{-5}
35.3	1.15×10^{-4}
40.0	4.62×10^{-4}
50.0	2.51×10^{-3}

The energy of activation, ΔE_a, was found to be 41.7 kcal./mole from a plot of log k *vs.* $1/T$.

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[1] S. M. Jorgensen, *J. prakt. Chem.*, **39**, 18 (1889); **41**, 449 (1890).

[2] Ethylenediamine is designated as en.

[3] J. C. Bailar, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 223.