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, moles H$_2$O / moles NaBH$_4$	$-\Delta H$, cal. / 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

$$NaBH_4(c) + 350H_2O(e) = NaBH_4 \cdot 350H_2O \quad (1)$$

$$\Delta H = -709 \pm 5 \text{ cal.}$$
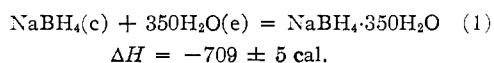
The most probable systematic error would be due to the presence of a sodium borate; 0.5 weight % Na$_2$B$_4$O$_7$·5H$_2$O would make the above value 10 cal. too positive. To correct to infinite dilution, we shall assume that the heat of dilution is the same as that for NaBr given by Harned and Owen[5] and shall ignore the effect of the 0.0124 M NaOH in the solutions. Hence for the reaction

$$NaBH_4(c) = Na^+ + BH_4^- \quad (2)$$

$$\Delta H^\circ_{298} = -776 \text{ cal.}$$
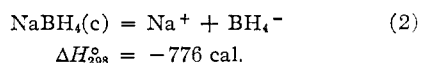
Since the heats of dilution of NaBr and NaI differ by only 10 or 20 cal. over this range,[6] it seems probable that this value is reliable within these limits.

Applying a correction for the present best value for the heat of formation of H$_3$BO$_3$·∞H$_2$O, −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.,

(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.

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]

(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

BY DANIEL T. HAWORTH, EDWARD F. NEUZIL AND SCOTT L. KITTSLEY

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)$_2$Cl$_2$]Cl.[2]

trans-[Co(en)$_2$Cl$_2$]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.