Vol. 80

Gel'bshstein, et al.12 None of these rate expressions account for the observation that the rate of exchange and the rate of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> hydrolysis are nearly equal in concentrated phosphoric acid solution.

## Appendix

The activity of water in phosphoric acid solutions at  $100^{\circ}$  was calculated from vapor pressure data.13,14 The activity of H3PO4 was calculated from the water activity by the usual method 15 modified to include three components because of the presence of appreciable amounts of  $H_4P_2O_7$  in the concentrated solutions. The modified relationship is

$$\ln \frac{a_1}{a_1'} = \int_{N_w'}^{N_w} \frac{(2N_w + N_1 - 1)}{(2N_w + N_1 - 2)} \,\mathrm{d} \ln a_w \qquad (11)$$

in which a and N refer to activity and mole fraction, respectively, the subscripts 1 and w denote the quantities for  $H_3PO_4$  and  $H_2O_5$ , respectively, and the primes denote the quantities at the selected

(12) A. I. Gel'bshstein, G. G. Shcheglova and M. I. Temkin, Akad. Nauk Doklady, SSSR, 107, 108 (1956).

(13) "Phosphorus, Properties of the Element and Its Compounds," TVA, Chem. Eng. Rep. No. 8, Wilson Dam, Alabama, 1950, p. 45.

(14) M. M. Striplin, Jr., Ind. Eng. Chem., 33, 910 (1941).
(15) I. M. Klotz, "Chemical Thermodynamics," Prentice-Hall, Inc., New York, N. Y., 1950, p. 296.

reference point  $N_1 = 0.05$ . The integration was performed graphically. Table VI gives the results.

	TABLE $VI$	
	Activities at 100°	
$(H_3PO_4),$	a <sub>w</sub> <sup>a</sup>	$a_1 b$
6.0	0.770	0.355
8.0	. 625	1.09
10.0	. 480	2.75
12.0	.315	7.70
14.0	.158	20.1
15.0	.102	29.3
16.0	.061	40.8
17.0	.0360	51.0
17.5	.0230	57.8
18.0	.0135	63.0
18.5	.00667	67.0

<sup>a</sup> Water is the standard state. <sup>b</sup> Relative values;  $a_1'$  (at  $N_1 = 0.05$ ) arbitrarily taken as 0.05.

The values at  $100^{\circ}$  of the constants appearing in the various rate expressions are

 $k_1 = 3.8 \ (10^{-5})$  g. atom/l. sec.  $k_2 = 2.4 \ (10^{-7})$  g. atom/l. sec.  $k_3 = 4.5 \ (10^{-12})$  g. atom/l. sec.  $k_4 = 1.4 \ (10^{-5})$  sec. <sup>-1</sup>  $k_5 = 2.1 \ (10^{-5}) \text{ g. atom/l. sec.}$  $k_6 = -5.33$ 

ST. LOUIS, MISSOURI

# [CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA RADIATION LABORATORY]

# The Heats of Formation at 25° of the Crystalline Hydrides and Deuterides and Aqueous Hydroxides of Lithium, Sodium and Potassium<sup>1</sup>

# BY STUART R. GUNN AND LEROY G. GREEN

# **Received September 19, 1957**

The heats of reaction with water have been measured at 25° for lithium, sodium and potassium and for their hydrides and The heats of reaction with watch have been measured as  $2.5 \text{ for hindright solution and potassimily and for high hybrid sine determined, in kcal./mole, are: M(c) + 1001 H<sub>2</sub>O(1) = MOH 1000H<sub>2</sub>O + <math>\frac{1}{2}\text{H}_2(g)$ ,  $\Delta H^0_{\text{Li}} = -53.142 \pm 0.019$ ,  $\Delta H^0_{\text{Na}} = -44.069 \pm 0.006$ ,  $\Delta H^0_{\text{K}} = -46.900 \pm 0.010$ ; MH(c) + 1001H<sub>2</sub>O(1) = MOH 1000H<sub>2</sub>O + H<sub>2</sub>(g),  $\Delta H^0_{\text{Li}} = -31.476 \pm 0.018$ ,  $\Delta H^0_{\text{Na}} = -30.582 \pm 0.019$ ,  $\Delta H^0_{\text{K}} = -33.081 \pm 0.005$ ; MD(c) + 1001H<sub>2</sub>O(1) = MOH 1000H<sub>2</sub>O + HD(g),  $\Delta H^0_{\text{Li}} = -31.321 \pm 0.007$ ,  $\Delta H^0_{\text{Na}} = 30.693 \pm 0.004$ ,  $\Delta H^0_{\text{K}} = -33.625 \pm 0.004$ . The thermochemical crystal energies are calculated and compared with electrostatic crystal energies.

There are few data in the literature concerning the heats of formation of the isotopic metal hydrides. The only calorimetric values are those for uranium hydride, deuteride and tritide, determined by Abraham and Flotow.<sup>2</sup> Sollers and Crenshaw have investigated the dissociation pressures of the hydrides and deuterides of sodium and potassium.<sup>3,4</sup> For both of the elements, the dissociation pressure of the deuteride is greater than that of the hydride, and the heats of formation calculated from the temperature coefficients in the vicinity of 300° are, in kcal./mole, NaH, -14.44; NaD, -15.80; KH, -14.15; KD, -14.45. Tronstad and Wergeland<sup>5</sup> report that the dissociation pressure of LiH is greater than that of LiD.

(1) This work was performed under the auspices of the U.S. Atomic Energy Commission.

(2) B. M. Abraham and H. E. Flotow, THIS JOURNAL, 77, 1446 (1955).

(4) E. F. Sollers and J. L. Crenshaw, ibid., 59, 2015 (1937).

(5) L. Tronstad and H. Wergeland, Kgl. Norske. Videnskab. Selskab, Forh., 10, No. 10, 36 (1937).

The purpose of this investigation was to secure accurate thermochemical values of the heats of formation of the crystalline alkali metal hydrides and deuterides in order that the effect of isotopic substitution upon the lattice energy might be compared with the difference in electrostatic energy resulting from the changed lattice spacing. The procedure consisted of measurement of the heats of reaction of the metals, hydrides and deuterides with water, the heat of formation of the hydrides and deuterides then being calculated from the difference in the heats of reaction. From the heats of hydrolysis of the metals, the heats of formation of the aqueous hydroxides, and consequently also of the aqueous metal ions, were determined with a precision considerably greater than previously has been reported.

## Experimental

The Calorimeter .-- The calorimeter used in this work is described in greater detail elsewhere.6 It consists of a gold-

(6) S. R. Gunn, Rev. Sci. Instruments, 29, 377 (1958).

<sup>(3)</sup> E. F. Sollers and J. L. Crenshaw, ibid., 59, 2724 (1937).

plated copper bomb having an internal volume of 675 ml. and suspended by means of Nylon cords in an evacuated submarine immersed in a thermostat. Stirring is effected by rocking the assembly through an angle of about 150°. The sample is contained in a glass bulb which is broken by a spring-loaded hammer whose action is initiated by rotating the submarine 90° beyond its normal limit. Temperature is measured with a Leeds and Northrup calorimetric platinum resistance thermometer, G-2 Mueller bridge, Liston-Becker breaker-amplifier and Bristol recorder. Duplicate calibrations are performed following each run. The calorimeter is cooled to the initial temperature (25.00°) of the run, and current is passed through a heater from a precisionregulated d.c. power supply. The power is measured with a Rubicon type B potentiometer, and standard resistors and cells are compared with N.B.S. standards. The length of the heating period is controlled by relays operated from a standard clock. Duplicate calibrations for the runs reported in this paper agreed, on the average, within 0.02%.

this paper agreed, on the average, within 0.02%. Materials.—All manipulations of materials were performed either in evacuated apparatus or in an evacuable argon-atmosphere glove box.

Lithium metal was purified by vacuum fusion and distillation. Eimer and Amend C.P. lithium containing about 1%sodium was used for preparation A and Maywood low sodium grade containing about 0.01% Na was used for the remainder. About 12 g. of lithium from which the storage oil had been removed with petroleum ether was placed in an Armco iron pot and heated at  $400^\circ$  for 4 hr. The pot was then assembled in a still employing an Armco iron condenser and receiver and distilled from  $900^\circ$  for 4 hr. Flame photometric analysis of preparation A showed 0.026% Al and 0.072% Na; spectrographic analysis showed 0.01% Al and 0.072% Na; m B, <0.01% Al and 0.01% Na in C; Ba, Ca, Cd, Cr, Fe, K, Mg, Pb, Sn and Zn were undetectable in all preparations. In preparation D, the lithium was fused in a separate apparatus at  $400^\circ$  and then forced through a 10-micron stainless steel filter with argon pressure. The filtrate was melted in the dry box, skimmed and poured into the distillation pot. This was heated under vacuum to  $500^\circ$ , cooled, returned to the dry box, and the surface again was cleaned. These precautions were found necessary to obtain a surface sufficiently clean to permit reasonable distillation rates at  $600^\circ$  where less lithium oxide was volatilized. The distillation was performed at  $600^\circ$  for 44 hr.

Lithium hydride was prepared by direct reaction of molten lithium with gaseous hydrogen at one atmosphere pressure. Preparations A and B used metal from the procedure of metal preparation B; preparation C used metal from the procedure of preparation D. The metal was placed in an Armco iron crucible. Hydrogen was purified by passing through a liquid nitrogen trap and over uranium at  $350^\circ$ . In preparations A and B, the temperature was raised to  $720^\circ$ , most of the hydrogen being absorbed in about 1 hr. Then it was lowered slowly to  $680^\circ$  and held there for 16 hr., lowered to  $500^\circ$  and held 20 hr., and then lowered in  $100^\circ$ steps with half-hour halts. In preparation C, the temperature was raised to  $725^\circ$ , slowly lowered to  $650^\circ$  and held 15 hr. and then lowered to  $500^\circ$  and held at that temperature for 65 hr. The product fractured readily into clear, very slightly bluish crystals several millimeters in length. Samples were stored in the dark.

Lithium deuteride was prepared by a procedure similar to that for the hydride, and the product was of similar appearance. The D:H mole ratio in two samples of preparation C was determined by pyrolysis to hydrogen, oxidation to water and nuclear magnetic resonance measurement; it was found to be 99.5:0.5.

Sodium (Baker and Adamson reagent grade) metal was purified by filtration and distillation in a Pyrex apparatus. About 12 g. of metal was placed on a coarse-grade sintered filter, melted under vacuum and forced through the filter with argon pressure. The apparatus was then re-evacuated and sealed off below the filter. The sodium was distilled at 460° for 4 hr. through a sidearm and condenser into a receiver bulb which was then sealed off and subsequently broken in the dry box. A single preparation was used for all calorimetric runs, spectrographic analysis showed 0.01% Al, 0.005% Ca, 0.01% Cu and 0.005% Mg; Ba, Cd, Cr, Fe, K, Li, Ni, Pb, Si and Sn were undetectable.

Sodium hydride was prepared by the evaporation of sodium in a hydrogen atmosphere. The apparatus consisted of a cylindrical Armco iron vessel having a lid fitted with a viewing port and two vacuum valves, one of which connected to an iron tube located in the center of the vessel and extending to within about 2 in. of the bottom. The valves were connected to a vacuum line, to a supply of purified hydrogen and to an all-glass solenoid-actuated pump which circulated hydrogen in through the re-entrant tube and out at the top. About 10 g. of sodium was loaded into the bottom of the reactor which was then sealed, evacuated and filled with hydrogen maintained at a pressure slightly greater than one atmosphere. A furnace was placed around the lower 4 inches of the reactor and the temperature raised to 750-790°, as measured by a thermocouple near the reactor wall; the actual temperature inside the vessel would be considerably lower. Hydrogen was circulated at 1-2 l. min.<sup>-1</sup> for 2-4 hr. until a thin mat of needle-like crystals formed across the reactor about midway in height. The circulation was then increased to 7 l. min.<sup>-1</sup> and continued 40 hr. The product was formed in a thick mat; it was fairly dense, chalk-like, and almost pure white at the center, with "whisof gray material above and below and with some very kers" small droplets of unreacted metal on the lower side. About 3 g. of material of good appearance was obtained in each run and pelleted in a 1/4 in. Parr press.

Solium deuteride was prepared by a procedure similar to that for the hydride. The deuteride seemed to form more slowly than the hydride, considerable metal being deposited with the deuteride when the same conditions were used. Accordingly, the runs were performed at 700° for 70–120 hr. to obtain 2–3 g. of usable material. Mass spectrometric determination of the D:H mole ratio in the gas from runs 1 and 2 indicated a value of 97:3 for this ratio in the original sample.

Potassium metal was obtained from the Callery Chemical Company. Spectrographic analysis showed 0.02% Al, 0.03% Fe and 0.03% Si; Ba, Ca, Cd, Cr, Li, Mg, Ni, Pb, Sn and Zn were not detected. Flame photometric analysis showed less than 0.05% Na. The metal was melted, filtered and distilled in an apparatus similar to that used for sodium except that the distillate was introduced directly into the calorimeter bulbs by use of a movable sample collector.

Potassium hydride and deuteride were prepared by the same procedure as for sodium hydride. The temperature was 640-655° for the hydride and 600-605° for the deuteride; the duration of the run was 70 hr. for both. The D:H mole ratio in the deuteride was 98.5:1.5, determined by the same method as for lithium deuteride.

To estimate the free metal content of the hydride and deuteride preparations, a procedure was developed in which samples were leached with liquid ammonia and the color was compared visually with standards prepared by dissolving known amounts of sodium in liquid ammonia. The analysis showed about 0.05% free Na in NaH preparation A, 0.1% in NaH preparation B and 0.04% in both NaD preparations. A rather good correlation was found between the amount of dark streaks on the pellet and the free metal content; since the KH and KD preparations showed considerably less streaking than NaH and NaD, their free potassium content was assumed to be negligible. Leaching of crushed samples of LiH and LiD produced no coloration.

Gas Determination.—As a supplement to the weighing of the sample for the determination of the amount of reaction and to indicate the purity of the sample, the hydrogen evolved in each run was measured. Prior to the run, the calorimeter was loaded with 405 ml. of distilled water and degassed by pumping through liquid nitrogen traps on the vacuum line for four brief intervals separated by one 15minute and two 30-minute periods of agitation by rocking in the calorimeter submarine. This procedure removed 2-4 ml. of water and left about 10<sup>-6</sup> mole of gas in the calorim-Following the run, hydrogen was removed by the same eter. procedure and transferred to a water-jacketed buret by means of a Toepler pump connected to the calorimeter bomb through two traps loaded with steel balls and immersed in liquid nitrogen. Pressure was measured with a Gaertner cathetometer which could be read to 0.005 cm. Two burets, having volumes of 246.36 and 917.2 ml., were calibrated gravimetrically with mercury; the smaller was used only for the sodium metal runs. As a check on the performance of the system, six samples of high-purity (approx. 99.99%) magnesium were treated with dilute solutions of hydrochloric and sulfuric acids. The average volume of hydrogen meas-

ured was 100.00% of the theoretical, the average error of a single determination being 0.05%.

#### Results

The results are shown in Table I. The first column gives the run number, the second the preparation used and the third the mass of the sample in grams. The purity given in the fourth column is that determined from the gas analysis, corrected, in the case of sodium hydride and deuteride, for that evolved by the assumed free-metal content. The fifth column gives the calculated heats of reaction at constant pressure, obtained from the observed heats at constant volume by the addition of a  $\Delta nRT$  term. The defined thermochemical calorie, 4.1840 absolute joules, is used throughout.

Table I	
---------	--

CALORIMETRIC RESULTS						
Run	Prepa- ration	Wt., g.	Purity, %	$-\Delta H$ , kcal./mole		
			Lithium			
1	Α	0.2616	99.45	53.132		
2	Α	.2662	99.08	53.079		
3	в	. $2564$	99.75	53.110		
4	в	.2489	99.76	53.174		
5	C	.2286	99.21	53.169		
6	С	.2532	99.44	53.249		
7	D	.21292	99.89	53.109		
8	D	.20059	99.97	53.113		
				$53.142\pm0.019$		
			Sodium			
1	Α	0.4006	100.13	44.073		
2	Α	.3998	(>97.54)	44.088		
3	А	.4135	99.83	44.058		
4	Α	.3899	99.87	44.065		
5	А	.4577	99.71	44.061		
				$44.069 \pm 0.006$		
			Potassium			
1	А	1.6417	100.01	46.880		
<b>2</b>	Α	1.4053	99.99	46.898		
3	Α	1.1480	99.92	46.894		
4	А	1.0217	99.86	46.898		
5	в	1.4659	100.07	46.946		
<b>6</b>	в	1.1170	99.94	46.881		
				$46.900 \pm 0.010$		
		Li	thium hydride			
1	Α	0.2473	99.61	31.463		
2	Α	.2469	99.69	31.469		
3	Α	.2501	99.93	31.441		
4	В	.2538	99.78	31.519		
5	В	.2443	99.59	31.561		
6	С	.20059	100.01	31.455		
7	С	.21458	99.89	31.427		
				$31.476 \pm 0.018$		
		Sc	dium hydride			
1	Α	0.4010	98.74	30.615		
2	А	.4389	98.20	30.679		
3	Α	.4553	99.17	30.534		
4	В	.5135	99.80	30.560		
$\overline{5}$	в	.4829	99.82	30.564		
6	в	. 4767	99.80	30.567		
7	в	.4850	99.76	30.556		
				$30,582 \pm 0,019$		

Potassium hydride					
1	А	0.8758	99.50	33.093	
2	Α	.7717	99.65	33.071	
3	Α	.8692	99.71	33.083	
-1	Α	.8414	99.74	33.072	
5	В	. 8904	99.60	33.069	
6	В	.8685	99.68	33.097	
				$33.081 \pm 0.005$	
		Lithiun	n deuteride		
1	Α	0.2758	99.71	31.306	
2	В	.24089	100.01	31.348	
3	В	.22548	100.08	31.315	
4	В	.24882		31.307	
$\overline{5}$	В	.25816		31.332	
б	С	.275		31.317	
				$\overline{31.321} \pm 0.007$	
		Sodi	um deuteride		
			00 01	20 684	
1	A	0.4319	99.61	30.004	
$\frac{1}{2}$	A A	0.4319 .4186	99.61 99.75	30.697	
1 2 3	A A B	0.4319 .4186 .5100	99.61 99.75 99.73	30.697 30.700	
1 2 3 4	A A B B	0.4319 .4186 .5100 .5199	99.61 99.75 99.73 99.79	30.697 30.700 30.686	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5     \end{array} $	A A B B B	0.4319 . 4186 . 5100 . 5199 . 4720	99.61 99.75 99.73 99.79 99.76	30.697 30.700 30.686 30.697	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5     \end{array} $	A B B B	0.4319 .4186 .5100 .5199 .4720	99.61 99.75 99.73 99.79 99.76	$30.697 30.697 30.686 30.697 \overline{30.693} \pm 0.004$	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5     \end{array} $	A B B B	0.4319 .4186 .5100 .5199 .4720 Potase	99.61 99.75 99.73 99.79 99.76 sium deuterid	$30.697 30.700 30.686 30.697 30.693 \pm 0.004 de$	
1     2     3     4     5     1	A B B B	0.4319 .4186 .5100 .5199 .4720 Potas: 0.8611	99.61 99.75 99.73 99.79 99.76 sium deuterid 98.99	$30.697 30.697 30.686 30.697 30.693 \pm 0.004 4e 33.614$	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2     \end{array} $	A B B B A A	0.4319 .4186 .5100 .5199 .4720 Potas: 0.8611 .7993	99.61 99.75 99.73 99.79 99.76 sium deuterid 98.99 99.19	$30.697 30.697 30.686 30.697 30.693 \pm 0.004 ie 33.614 33.637$	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3     \end{array} $	A B B B A A B	0.4319 .4186 .5100 .5199 .4720 Potas: 0.8611 .7993 .8816	99.61 99.75 99.73 99.79 99.76 sium deuterid 98.99 99.19 99.90	$30.697 30.697 30.686 30.697 30.693 \pm 0.004 ie 33.614 33.637 33.624$	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4     \end{array} $	A B B B A A B B B	0.4319 .4186 .5100 .5199 .4720 Potas: 0.8611 .7993 .8816 .9258	99.61 99.75 99.73 99.79 99.76 sium deuterid 98.99 99.19 99.90 99.84	$30.697 30.697 30.697 30.693 \pm 0.004$ fe 33.614 33.637 33.624 33.629	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       5 \\       1 \\       1 \\       2 \\       3 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       1 \\       2 \\       3 \\       4 \\       5 \\       1 \\       5 \\       1 \\       1 \\       2 \\       3 \\       1 \\       5 \\       1 \\       2 \\       3 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       2 \\       3 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\       5 \\       1 \\     $	A B B B B A A B B B B	0.4319 .4186 .5100 .5199 .4720 Potas: 0.8611 .7993 .8816 .9258 .8645	99.61 99.75 99.73 99.79 99.76 sium deuterid 98.99 99.19 99.90 99.84 99.81	$30.697$ $30.697$ $30.697$ $30.693 \pm 0.004$ fe $33.614$ $33.637$ $33.624$ $33.619$	

There was considerable evidence that in breaking the bulb into which the sodium was distilled and by removing the metal, particles of glass became mixed with the metal. The amount of reaction is therefore calculated only from the gas determination, and the purity figures represent merely lower limits. In the case of potassium, the samples were of uniformly high purity, and the average of the sample weight and gas determination was used to determine the amount of reaction. In the lithium runs, the impurity was assumed to be  $Li_2O$ , and a heat correction for this was applied. In all the hydride and deuteride runs, except for sodium hydride and sodium deuteride, a heat correction was applied on the assumption that the impurity was the corresponding hydroxide. Sodium hydride preparations A and B were assumed to include 0.05% Na and 0.1% Na, respectively, and both sodium deuteride preparations were assumed to include 0.04% Na. The effect of this procedure is to weight the gas determination considerably more heavily than the weighing when determining the amount of reaction. The values for runs 4 and 5 of LiD are calculated from sample weights only, and that for run 6 of LiD, from the gas analysis only. The deuteride results are corrected to 100% isotopic purity. The heat values are corrected to a final concentration of MOH · 1000H<sub>2</sub>O, using heat of dilution data from the NBS tables.7 The actual

(7) F. D. Rossini, et al., "Selected Values of Chemical Thermo-dynamic Properties," Circular of the National Bureau of Standards, No. 500 (1952).

	This work	Ketchen and Wallace <sup>8,9</sup>	Messer, Fasolino and Thalmayer <sup>10</sup>	NBS7
$LiOH \approx H_2O$	$-121.572 \pm 0.019$		$-121.42 \pm 0.11$	-121.511
$NaOH \propto H_2O$	$-112.483 \pm .006$	$-112.37 \pm 0.10$	$-112.55 \pm .13$	-112.236
$\mathrm{KOH} \simeq \mathrm{H_2O}$	$-115.323 \pm .010$	$-115.21 \pm 0.12$	$-115.37 \pm .10$	-115.00
LiH(c)	$-21.666 \pm .026$		$-21.34 \pm .15$	-21.61
LiD(c)	$-21.784 \pm .021$			
NaH(c)	$-13.487 \pm .020$		$-13.60 \pm .27$	- 13.7
NaD(c)	$-13.339 \pm .007$			
KH(c)	$-13.819 \pm .011$		$-15.16 \pm .16$	-13.6
KD(c)	$-13.238 \pm .011$			

 Table II

 Heats of Formation at 25° (in Kcal./Mole)

final mole ratios ranged from 590 to 1330. All calorimetric reactions were initiated at  $25.00 \pm 0.04^\circ$ , and the heat values refer to the isothermal reactions at this temperature.

Using these data together with the NBS values for the heats of formation of H<sub>2</sub>O and HD and the heats of dilution of the hydroxides, the standard heats of formation of the aqueous hydroxides and of the crystalline hydrides and deuterides are calculated. These are shown in Table II, together with some earlier values. The best previous data on these reactions are probably those for the heats of hydrolysis of sodium and potassium that were measured by Ketchen and Wallace<sup>8,9</sup> and those for the heats of hydrolysis of lithium, sodium and potassium and their hydrides that were measured by Messer, Fasolino and Thalmayer.<sup>10</sup> These workers have discussed earlier investigations. The statistical precisions given in Table II are the standard deviations  $(\sqrt{\Sigma d^2/n(n-1)})$  of the reaction measurements and do not include errors contributed in the heats of formation of H<sub>2</sub>O and HD and in the heats of dilution of the hydroxides.

The three sets of values for the heats of hydrolysis of sodium and potassium agree within the statistical precision of each. Compared with the earlier work, the present technique would seem to offer two distinct advantages: (1) use of a moving reaction bomb assures chemical and thermal equilibrium within and between the liquid and gas phases and (2) determination of the amount of reaction by measurement of the evolved hydrogen as well as weighing of the metal, permits detection of, and correction for, errors due to hydroxide or other impurity.

The alkali metal hydrides have the NaCl structure; the lattice constants of some samples of the preparations used in this work were determined in this Laboratory<sup>11</sup> and are given in Table III. The electrostatic energy of a NaCl-type crystal may be calculated from the expression

$$U_{\rm E} = \frac{N\alpha e^2}{R_0}$$

where N is Avogadro's number,  $\alpha$  is the Madelung constant, e is the electronic charge and  $R_0$  is the nearest-neighbor distance. Using the values N = $6.02380 \times 10^{23}$ ,  $\alpha = 1.747558$  and  $e = 4.80223 \times$ 

(8) E. E. Ketchen and W. E. Wallace, THIS JOURNAL, 73, 5810 (1951).

(9) E. E. Ketchen and W. E. Wallace, *ibid.*, **76**, 4736 (1954).

10<sup>-10</sup> e.s.u., as given by Rossini,<sup>12</sup> Sherman<sup>13</sup> and Rossini,<sup>12</sup> respectively, the energy in kcal. per mole is

$$U_{\rm E} = \frac{1160.45}{a}$$

where a is the lattice constant in angströms; this quantity is presented in the third column of Table III.

		<b>Fable III</b>	
	Crys	TAL ENERGIES	
	Lattice constant, Å.	$U_{\rm E}$ , kcal./mole	U, kcal./mole
LiD	$4.069 \pm 0.001$	$285.19 \pm 0.07$	218.76
LiH	$4.083 \pm .001$	$284.22 \pm .07$	217.76
		$0.97 \pm 0.10$	$1.00 \pm 0.04$
NaD	$4.867 \pm .001$	$238.43 \pm 0.05$	193.47
NaH	$4.879 \pm .001$	$237.85 \pm .05$	192.74
		$0.58 \pm 0.07$	$0.73 \pm 0.03$
KD	$5.696 \pm .001$	$203.73 \pm 0.04$	170.42
KH	$5.708 \pm .001$	$203.30 \pm .04$	170.12
		$0.43 \pm 0.06$	$0.30 \pm 0.02$

The experimental values for the crystal energy at 25° may be calculated from the present and other data. The heats of formation of the gaseous alkali ions are taken from the NBS tables. The electron affinities of hydrogen and deuterium at 0°K. are taken from the calculations of Hylleraas and Midtal<sup>14</sup> and modified by the mass polarization correction of Hart and Herzberg<sup>15</sup> are, respectively, -17.373 and -17.384 kcal./mole. These values, together with the heat of dissociation and enthalpy data given by Woolley, Scott and Brickwedde,<sup>16</sup> yield the values 33.234 and 34.116 kcal./mole for the standard heats of formation at 25° of H<sup>-</sup>(g) and D<sup>-</sup>(g), respectively. The thermochemical crystal energy U defined as  $-\Delta H^0_{298}$  for the reaction

$$M^{+}(g) + H^{-}(g) = MH(c)$$

is given in the fourth column of Table III.

It may be seen that the differences in U and  $U_{\rm B}$  for the hydrides and deuterides agree fairly closely, within experimental error. If the data are treated by the Born equation

$$U = U_{\rm E} \left( 1 - \frac{1}{n} \right)$$

- (12) F. D. Rossini, et al., THIS JOURNAL, 74, 2699 (1952).
- (13) J. Sherman, Chem. Revs., 11, 93 (1932).
- (14) E. A. Hylleraas and J. Midtal, Phys. Rev., 103, 829 (1956).
- (15) J. F. Hart and G. Herzberg, *ibid.*, 106, 79 (1957).
- (16) H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Research Natl. Bur. Standards, 41, 379 (1948).

<sup>(10)</sup> C. E. Messer, L. G. Fasolino and C. E. Thalmayer, *ibid.*, 77, 4524 (1955).

<sup>(11)</sup> A. Zalkin and V. Silveira, unpublished work.

it would seem that n is slightly larger for the deuterides. The present values of U for LiH and LiD may be

compared with those of Kapustinsky, Shamovsky

absorption spectra of LiH and LiD and, attributing the band to the process

LiH(c) + Li(g) + H(g)

derived 219.2 and 220.8 kcal./mole for  $U_{\text{LiH}}$  and  $U_{\text{LiD}}$ , respectively. LIVERMORE, CALIF.

and Bayushkina<sup>17</sup> who measured the ultraviolet (17) A. F. Kapustinsky, L. M. Shamovsky and K. S. Bayushkina, *Acta Physicochim. U.R.S.S.*, **7**, 799 (1937).

[CONTRIBUTION NO. 74 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

# 2-Butanethiol: Chemical Thermodynamic Properties between 0 and 1000°K.; Rotational Conformations<sup>1</sup>

# By J. P. McCullough, H. L. Finke, D. W. Scott, R. E. Pennington, M. E. Gross, J. F. Messerly and Guy Waddington

## RECEIVED APRIL 24, 1958

The chemical thermodynamic properties of 2-butanethiol in the ideal gaseous state (0 to 1000°K.) were calculated by use of calorimetric, spectroscopic and molecular structure information. The thermodynamic and spectroscopic results show that 2-butanethiol exists as a mixture of molecules in three distinct rotational conformations—two with about equal energies and a third with about 1.0 kcal. mole<sup>-1</sup> higher energy. Experimental studies provided the following information: values of heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 307°K.) and the vapor (346 to 453°K.); the triple point (318 to 358°K.); parameters of the equation of state; vapor pressure (38 to 121°); and standard heat of formation at 298.16°K.

Thermodynamic investigations of organic sulfur compounds are made in this Laboratory as part of American Petroleum Institute Research Project 48. Comprehensive studies have been made of all seven isomeric  $C_4H_{10}S$  thiols and sulfides to determine accurately the effect of molecular structure on thermodynamic properties as well as to provide useful data for each isomer. Results obtained for six of the isomers have been published.<sup>2</sup> The present paper reports results for the racemic mixture of 2butanethiol (*sec*-butylmercaptan), the only one of the  $C_4H_{10}S$  isomers for which optical isomerism is possible.

The experimental part of this investigation included studies by low temperature calorimetry, vapor flow calorimetry, comparative ebulliometry and combustion calorimetry. The detailed results are given later in the Experimental section. The results needed for calculating thermodynamic properties, as discussed in the next section, are collected in Table I.

## Calculation of Thermodynamic Properties

Thermodynamic functions were calculated by standard methods of statistical mechanics and thermodynamics. Most of the parameters needed were obtained from spectroscopic and molecular structure information; the few remaining were chosen so as to obtain agreement with the observed values of entropy and heat capacity in Table I. The calculated thermodynamic functions and the

(1) This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) (a) D. W. Scott, J. P. McCullough, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp, H. L. Finke and Guy Waddington, THIS JOURNAL, 80, 55 (1958), and earlier publications cited therein; (b) W. N. Hubbard, W. D. Good and Guy Waddington, *J. Phys. Chem.*, **62**, 611 (1958). observed value of the heat of formation in Table I were used in calculating the standard heat, standard free energy and equilibrium constant of formation at selected temperatures between 0 and 1000°K.

## TABLE I

Observed and Calculated Molal Thermodynamic Properties of 2-Butanethiol in the Ideal Gaseous State

Entr	opy, S°, cal.	deg. ~1	Heat capad	city, C <sub>p</sub> °, ca	l. deg1
<i>T</i> , °K.	Obsd.	Calcd.	<i>T</i> , °K.	Obsd.	Calcd.
298.16	87.67	87.65	346.2	31.83	31.82
318.0	89.57	89.52	368.2	33.29	33.30
328.6	90.54	90.51	403.2	35.56	35.58
336.7	91.27	91.26	453.2	38.68	38.68
358.1	93.22	93.23			

4C(c, graphite) +  $5H_2(g)$  +  $1/_2S_2(g)$  = C<sub>4</sub>H<sub>10</sub>S(g). Heat of formation,  $\Delta H f^{\circ}_{28,16}(\text{obsd.})$  =  $-38.39 \pm 0.19$  kcal.

Vibrational Assignment.—Available spectroscopic data for 2-butanethiol are collected in Table II.<sup>3-5</sup> The data of ref. 4 and 5 were obtained with samples of the same highly purified material used in this research.

Three spectroscopically distinguishable rotational conformations of 2-butanethiol are possible, as shown in Fig. 1. The conformation with the ethyl group gauche to the thiol group and trans to the methyl group is labeled A; that with the ethyl group trans to the thiol group and gauche to the methyl group is labeled B; and that with the ethyl group gauche to both the thiol and methyl groups is labeled C. From considerations of the energy relationships among the rotational conformations of 1-

<sup>(3)</sup> K. W. F. Kohlrausch and F. Köppl, Monatsh., 63, 255 (1933).

<sup>(4)</sup> American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 229.

<sup>(5)</sup> Ref. 4, Catalog of Infrared Spectral Data, Serial Nos. 1545 and 1622.