under (a).[8] For assumption (b), $k_1' = K_1'/2$, $k_3' = 2K_2'$, $k_1'' = K_1''/2$, and $k_3'' = 2K_2''$, and the pk values are given in Table I. For assumption (c), $k_1' = K_1'$, $k_3' = K_2'$, $k_1'' = K_1''$ and $k_3'' = K_2''$ if HP is the predominant isomer. The pk values obtained by this assumption are the same as the pK values.

This analysis of the hemoglobin data is closely related to that which has been applied in the interpretation of the pH dependence of the forward and reverse reactions catalyzed by fumarase.[9] The values of pK_1 and pK_2 for fumarase in 0.01 M acetate buffer at 25° are 6.2 and 6.8. When fumarate forms a complex with the enzyme pK_1 is reduced to 6.3 and pK_2 is raised to 7.3. When l-malate forms a complex with the enzyme pK_1 is raised to 6.6 and pK_2 is raised to 8.4.

It is not to be expected that the values of pK_1', pK_2', pK_1'' and pK_2'' will be constant over a wide range of pH. They are not thermodynamic constants for the hemoglobin molecule, but are rather group constants which will vary with the net charge on the hemoglobin molecule.[10,11] The result of the electrostatic effect of the other charged groups is to increase the apparent pK values as the pH is increased above the isoelectric point and to decrease them as the pH is decreased below the isoelectric point. Estimates of the electrostatic effect calculated in the usual way[12,13] show that they are large enough to be taken into consideration for hemoglobin and indicate the need for further research on the pK values of the heme-linked groups of hemoglobin.

[8] The designation of pk_1 and pk_2 used here is the reverse of Wyman's. The change is made so that pk_1 refers to the more strongly acidic group.

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The Heats of Formation of Lithium, Sodium and Potassium Hydrides

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As a part of a general study of the physical and thermodynamic properties of light metal hydrides, we have reinvestigated the heats of formation of lithium and sodium hydrides, and have measured the heat of formation of potassium hydride calorimetrically for the first time.[2] The uncertain purity of many of the earlier hydride preparations makes such reinvestigation desirable.

The thermochemical method used was the standard one, involving the determination of the difference between the heat of hydrolysis of the hydride and that of the corresponding metal, both measured in the same calorimeter. The calorimeter was of the bomb type, the evolved hydrogen from the hydrolysis being confined. Ketchen and Wallace[3] and Rengade[4] discuss the objections to the open type of calorimeter for this type of reaction.

Experimental

The apparatus and technique closely resemble those employed in measuring heats of combustion of organic compounds. The bomb was surrounded by 2000 ml. of water inside the Daniels adiabatic jacket of an Emerson bomb calorimetric apparatus. Temperature measurements were made to a precision of 0.001° by means of a Leeds and Northrup platinum resistance thermometer, Bureau of Standards calibrated, and a Leeds and Northrup Type G-2 Mueller bridge. The temperature difference between jacket and bomb was controlled manually, and indicated to 0.03° by means of a thermocouple and galvanometer.

The bomb was of Monel metal, with a volume of 625 ml. Its cover was pressed leaktight against the bomb by means of a threaded collar and a neoprene gasket, and was provided with a crushing rod system enabling sample capsules within the bomb to be crushed from the outside. Baffle plates with irregularly spaced holes prevented the reactants from being thrown to the top of the bomb by the violence of the reaction. A valve in the cover enabled preliminary evacuation of air and later release of evolved hydrogen.

The sample capsule, made by sealing off the material in a Pyrex test-tube of 150 mm. by 15 mm., was placed in the bomb with 150 ml. of water. Sample size was about 0.1 gram atom of metal, or 0.05 mole of hydride. It was established that the necessary evacuation of air before crushing removed 1.0 ± 0.5 g. of water. Final equilibration resulted 30–40 minutes after crushing. Corrections were made for heat losses of about 0.0005 to 0.001° per minute during the equilibrations.

Calibration and Units.—The water equivalent of the calorimeter was determined electrically by potential and current measurements on a Leeds and Northrup Type K potentiometer. The total energy equivalent of the calorimeter was 2626 ± 3 (standard deviation of the mean) cal. per degree, including 149 g. of water inside the bomb. The defined calorie, equal to 4.1840 absolute joules, was used.

Atomic weights employed were: Li 6.940, Na 22.997, K 39.100, and H 1.0080.

Materials.—Lithium metal from the Metalloy Corporation was trimmed of its coating under CO_2, and subjected to vacuum fusion in a stainless steel retort for four hours at 400° and 3 μ final pressure, to remove sodium. Sample capsules were filled and weighed under dry argon.

The sodium metal was J. T. Baker reagent grade, used without further purification. The sample capsules were prepared *in vacuo* using a technique which removed the oxide coating by fusion and led to almost mirror-like samples.

The potassium metal, furnished by the Callery Chemical Company, contained about 0.8% sodium by spectrographic analysis. It was used without further purification, correction being made for its sodium content. Capsules were filled by the same technique used for sodium.

Hydrogen for hydride synthesis was purified by passage through a Deoxo purifier, Drierite and a uranium metal getter at 500°.

Lithium hydride was synthesized by passing hydrogen over molten lithium at 720° and one atmosphere for 24 hours. The well-developed crystals were 1–3 mm. in size varying from white to light gray in color.

Sodium and potassium hydrides were made by passing hydrogen over the molten metal at one atmosphere and 650–750° and 600°, respectively. The products condensed as fine white to gray cottony masses on the cold part of the apparatus. The gray portions were rejected. Considerable difficulty was encountered in obtaining suitable samples of sodium hydride. Several preparations which either showed globules of metallic sodium or had abnormally low contents of active hydrogen were rejected. Since batch size was limited to 3–6 g., final measurements were performed on five batches

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[1] Based in part upon a thesis submitted by Ludwig G. Fasolino in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at Tufts College.

[2] I. Kasarnowsky and M. Proskurnin, *Z. Physik*, **43**, 512 (1927), report a very rough unpublished value of −9 kcal./mole.

[3] E. E. Ketchen and W. E. Wallace, THIS JOURNAL, **73**, 5810 (1951).

[4] E. Rengade, *Bull. soc. chim.*, [4] **3**, 188, 190 (1907).

containing 96.5% or better of theoretical hydrogen. These are designated by letters A through E in subsequent data.

All sample capsules of hydrides were prepared and weighed in dry nitrogen.

Analyses and Purity.—All samples except the sodium were analyzed spectrographically for other alkali metals and calcium. With the exceptions of about 0.8% Na in the potassium and 0.3% Na in the potassium hydride, all impurities of this type were present in less than 100 p.p.m.

Available hydrogen was determined by treating the hydride with a water–dioxane mixture, and measuring the volume of hydrogen evolved. The results follow, in per cent. of theoretical hydrogen.

LiH: (106.5), 100.3, 99.0, 98.3, 100.3, 99.3, (102.8), 101.2: 99.7 ±0.4

NaH: (A) 99.1, 100.6, 98.2, av. 99.3; (B) 97.8, 98.9, av. 98.4; (C) 98.4, 98.2, av. 98.3; (D) 96.5, 98.4, av. 97.5; (E) 96.0, 97.4, av. 96.7

KH: 105.1, 98.8, 101.9, 101.9, 103.6; 102.3 ±1.0

In calculating the energy evolved per mole, the energy equivalent of the calorimeter was corrected for the heat capacity of the product solutions inside the bomb using the data of Richards and Gucker[5] for NaOH, and of Richards and Rowe[6] for LiOH and KOH.

TABLE I

DATA ON HEATS OF HYDROLYSIS

Wt., g.	Cor. Δt°	Moles H_2O/ MOH	Init. t, °C.	ΔE per mole uncor.	Corrn. Diln.	Corrn. to 25°	Cor. ΔH, kcal.
Lithium Metal							
0.8493	2.451	68	24.07	−52.55	−0.40	−0.40	−52.70
.5980	1.733	96	22.50	−52.79	− .32	− .10	−52.92
.9697	2.815	59	24.44	−52.88	− .41	− .02	−53.01
1.0257	2.975	56	22.23	−52.81	− .41	− .12	−53.05
0.9117	2.650	63	22.89	−52.93	− .40	− .09	−53.12
.6503	1.891	88	23.08	−52.96	− .34	− .08	−53.08
.8206	2.395	70	21.85	−53.16	− .40	− .13	−53.39
.9384	2.747	61	22.44	−53.31	− .40	− .11	−53.52
Sodium Metal							
1.4215	1.060	134	26.29	−44.96	−0.14	+0.07	−44.73
1.0953	0.805	175	23.98	−44.34	− .14	− .05	−44.23
1.3257	.971	143	25.67	−44.22	− .14	+ .03	−44.03
1.2090	.894	157	27.65	−44.60	− .14	+ .13	−44.32
1.2230	.894	155	27.52	−44.09	− .14	+ .12	−43.81
1.5276	1.119	124	21.52	−44.23	− .13	− .18	−44.25
Potassium Metal							
3.0450	1.406	106	23.17	−47.35	−0.20	−0.10	−47.35
3.9202	1.813	82	21.45	−47.45	− .22	− .20	−47.58
4.0427	1.862	80	23.05	−47.23	− .22	− .12	−47.27
3.2269	1.482	100	22.63	−47.11	− .20	− .13	−47.15
3.3129	1.525	98	23.58	−47.22	− .20	− .08	−47.20
Lithium Hydride							
0.5298	0.807	124	25.28	−31.80	−0.29	+0.01	−31.49
.4517	.696	146	26.05	−32.12	− .28	+ .04	−31.76
.4116	.633	160	24.34	−32.08	− .27	− .03	−31.79
.4945	.758	133	22.45	−32.01	− .29	− .10	−31.82
.5591	.868	118	23.43	−32.38	− .30	− .06	−32.15
.5154	.784	128	22.92	−31.73	− .29	− .09	−31.53
Sodium Hydride							
A 0.7659	0.385	259	22.27	−31.65	−0.14	−0.14	−31.52
B .6373	.319	311	22.90	−31.54	− .14	− .01	−31.61
C .4627	.218	429	26.16	−29.67	− .13	+ .05	−29.57
C .9214	.442	215	25.07	−30.22	− .14	.00	−30.08
C 1.5159	.751	131	24.88	−31.19	− .14	.00	−31.17
D 1.2133	.579	164	21.98	−30.10	− .14	− .16	−30.43
D 0.9462	.458	210	21.85	−30.49	− .14	− .16	−30.82
D 1.1133	.539	178	22.66	−30.48	− .14	− .12	−30.78
E 0.8200	.392	242	26.10	−30.12	− .14	+ .05	−30.44
E 0.8496	.398	233	25.05	−29.51	− .14	.00	−29.86
Potassium Hydride							
1.7056	0.523	194	24.92	−32.25	−0.18	0.00	−31.83
1.8623	.573	178	24.20	−32.37	−0.18	− .04	−31.99
1.8589	.572	178	23.84	−32.36	− .18	− .06	−32.01
1.7615	.545	188	23.14	−32.55	− .18	− .10	−32.24
2.2194	.678	149	26.56	−32.11	− .19	+ .09	−31.61

Corrections to infinite dilution were made by means of the heats of formation of the aqueous hydroxides tabulated in NBS "Selected Values."[7] The corrections to 25° were made using the following heat capacities: for hydrogen, water and the metals, the NBS values[7]; for lithium hydride 8.2 cal./mole deg.[8]; for sodium and potassium hydrides, estimated values of 10 and 11 cal./mole deg., respectively; and for the aqueous hydroxides, the partial molal heat capacities at infinite dilution as calculated by Rossini.[9]

The values for sodium hydride were corrected for impurity based upon the hydrogen evolution data. Since water apparently was the most active contaminant, the assumption was made that the impurity was entirely sodium hydroxide. The heat of solution of the sodium hydroxide was taken from NBS "Selected Values."[7]

Results.—Table I gives the experimental data, corrections, etc., for the metals and the hydrides. The letters describing the sodium hydride runs are the batch designations previously mentioned.

Table II presents the final values for the heats of hydrolysis of the metals and the hydrides, and the heats of formation of the hydrides, along with comparisons with the results of other workers. The precisions indicated are the standard deviations.[10] Some of the earlier, less accurate results of other workers have been omitted for the metals. The earlier results given for lithium metal and lithium hydride have been recalculated to 25° and infinite dilution. The values previously recalculated by Bichowsky and Rossini[11] for 18° were used as starting values, and the previously given heat capacities were applied.

TABLE II

HEATS OF HYDROLYSIS AND FORMATION

ΔH, kcal./mole at 25°, infinite dilution

$$M(s) + H_2O(l) = MOH(\infty) + 1/2\ H_2(g)$$
$$MH(s) + H_2O(l) = MOH(\infty) + H_2(g)$$
$$M(s) + 1/2\ H_2(g) = MH(s)$$

	This research	Other results
Li, Hydrolysis	−53.10 ± 0.11	−53.58,[14] −53.1,[15] −53.22[16]
Na, Hydrolysis	−44.23 ± .13	−44.36,[4] −45.38,[17] −44.05[3,18]
K, Hydrolysis	−47.05 ± .10[12]	−46.78,[4] −46.89[3,16]
LiH, Hydrolysis	−31.76 ± .10	−31.97,[14] −31.62[16]
NaH, Hydrolysis	−30.63 ± .23	−25.8,[19] −31.57[20]
KH, Hydrolysis	−31.89 ± .12[13]	
LiH, Formation	−21.34 ± .15	−21.61,[14] −21.60[16]
NaH, Formation	−13.60 ± .27	−16.6,[19] −12.8,[20] −13.7[7] −13.9,[21] −14.44[22]
KH, Formation	−15.16 ± .16	−9,[2] −13.6,[7] −14.24,[21] −14.15[22]

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[5] T. W. Richards and F. T. Gucker, THIS JOURNAL, **51**, 712 (1929).

[6] T. W. Richards and A. W. Rowe, *ibid.*, **43**, 770 (1921).

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(9) F. D. Rossini, *J. Research Natl. Bur. Standards*, **7**, 47 (1931).

(10) The "uncertainty interval," which F. D. Rossini and W. C. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939), have proposed as a standardized estimate of the reliability of a calorimetric mean value, is twice the standard deviation.

(11) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Thermochemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

(12) A correction for sodium impurity, of +0.26 ± 0.05 kcal./mole, was applied.

(13) A correction for sodium content (assumed to be sodium hydride) of +0.05 ± 0.02 kcal./mole, was applied.

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(20) H. Hagen and A. Sieverts, *Z. anorg. allgem. Chem.*, **185**, 254 (1929).

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Discussion.—The results on the alkali metals agree satisfactorily with the best previously published values, to within 0.2–0.5%.

The results on lithium hydride agree fairly well, the present value of the heat of hydrolysis being the highest. This higher value is explained if the sample used in this research is somewhat purer than the samples of the earlier workers. Thus, the heat of formation of lithium hydride seems to be established.

The heats of hydrolysis and formation of sodium hydride are less certain, owing to the relatively rapid rate of contamination of the finely divided samples by reaction with residual moisture in the dry-box atmosphere. The small batch size also necessitated the combination of data from several preparations, rather than their accumulation from one.

The heat of formation of sodium hydride of −13.60 kcal./mole agrees within experimental error with that of Hagen and Sieverts[20] of −12.8, which was probably obtained on a purer sample than that of de Forcrand.[19]

Most of the previously published values for sodium and potassium hydrides are based upon dissociation pressure data in the region of 300 to 350°. These are undoubtedly accurate to ±2% at these temperatures, but their extrapolation to 25° is uncertain in the absence of high temperature heat capacity data for the hydrides. These uncertainties may be mainly responsible for the discrepancies for these compounds shown in Table II.

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The Radiation-induced Oxidation of Ferrous Ion

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We should like to record our agreement with the remarks of Barr and King,[1] concerning the radiation chemistry of ferrous ion. We have also found[2] complete agreement between theory and experimental results if, in addition to the equations given previously,[3] Allen's "molecular yield" process[4]

$$2H_2O \longrightarrow H_2 + H_2O_2 \qquad (1)$$

is also taken into account. Furthermore, the mechanism which has been suggested[3] for the radiation-induced reaction in deaerated ferrous sulfate solutions has been confirmed by independent evidence obtained in a study of the photochemistry of ferrous sulfate solutions.[5]

In a recent paper, also dealing with the action of γ-rays on *deaerated* solutions of ferrous sulfate, Dewhurst[6] has found that the initial yield of the ferrous oxidation is dependent upon ferrous salt concentrations and upon pH; an inspection of his results shows that this is so only at relatively low ferrous salt concentrations ($[Fe^{2+}] < 5 \times 10^{-3}\ M$) and at $p\text{H} > 1$. It should be pointed out that our mechanism is fully capable of explaining these results. It must be borne in mind that the mathematical equations given in our paper for the case of deaerated solutions have been derived, as stated there, under the assumption that interactions of radicals such as

$$H + OH \longrightarrow H_2O \qquad (2)$$

and recombination of hydrogen atoms

$$2H \longrightarrow H_2 \qquad (3)$$

can be neglected. This assumption holds only when the ferrous salt and hydrogen ion concentrations are sufficiently high, and under these conditions excellent agreement is obtained with our kinetic equations. Under the conditions of Dewhurst's experiments (ref. 6), these interactions cannot always be neglected, as shown clearly by the dependence of the initial yield on the ferrous salt concentration. If, when appropriate, *e.g.*, the recombination of hydrogen atoms is taken into account, our theory leads directly to an explanation of the dependence of the initial yields on ferrous salt concentration and pH. (The pH dependence of the reaction in deaerated solutions can be interpreted on the basis of a mechanism involving the H_2^+ ions; calculations carried out by Coulson[7] have shown that the stability of this species in acid solution is fully compatible with theoretical expectations.)

In *aerated* ferrous sulfate solutions the situation regarding the initial pH effect is not quite as clear. Dewhurst's experiments show that the initial oxidation yield is quite independent of the hydrogen ion concentration down to concentrations of 5×10^{-2} M H_2SO_4. On the basis of the present theory an initial dependence at higher pH's, in a region of sufficiently low ferrous ion concentrations, may be due to interactions between the radicals in the clusters of high radical density, *e.g.*, $O_2^- + OH \rightarrow O_2 + OH^-$, with the dissociation equilibrium $HO_2 \rightleftarrows H^+ + O_2^-$. On the other hand, an initial pH dependence would also arise if a relatively large amount of ferric salt is initially present. The dependence of the oxidation yield on any ferric salt initially present is, of course, fully explained by our original mechanism, being simply due to the competition between the following two reactions

$$Fe^{2+} + HO_2 \longrightarrow Fe^{3+} + HO_2^- \qquad (4)$$

$$Fe^{3+} + O_2^- \longrightarrow Fe^{2+} + O_2 \qquad (5)$$

reaction (5) being favored as the pH is increased.

Further experiments at different pH and ferrous salt concentrations may be required to clear up this point. Otherwise all the experimental results can

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