fact that we have always had some alcohol present in our titrations, as carrier of the alcoholate, and even amyl alcohol has some dissociating power. Curiously enough, however, the addition of alcohol in larger amounts makes the end point of the titrations less sharp than when the amount of alcohol is kept at a minimum. We would emphasize that our titrations have been made with solutions of acid and alkali which have almost no conductivity, that the resulting salt solutions also have practically no conductivity, that the reaction is instant and that the action of the indicator does not differ materially from that observed in aqueous solutions.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 82.]

THE DISSOCIATION PRESSURES OF SODIUM AND POTASSIUM HYDRIDES.

BY FREDERICK G. KEYES.

Received March 23, 1912.

1. Review of Previous Investigations.

Gay-Lussac and Thénard[1] were the first to observe that metallic sodium and potassium absorb hydrogen. In the case of sodium no quantitative results were obtained. They observed, however, in the case of potassium, that one equivalent of the metal absorbed one-quarter of an equivalent of hydrogen.

Troost and Hautefeuille[2] studied the reaction and measured the equilibrium pressure of hydrogen over both the metals. They also attempted to determin the composition of the hydrides. The analysis was made by saturating a definit weight of metal and subsequently pumping out and measuring the hydrogen gas. No details of the experiments are given, but the formulas Na_2H and K_2H are assigned. Equilibrium measurements for both hydrides were made from 330° to 430°. The values will be presented below.

Henri Moissan[3] prepared both hydrides by heating the metals in a current of hydrogen gas. The excess of metal was then extracted from the product by means of liquid ammonia. The analysis of the hydrides thus obtained was made by decomposing the compounds with water and measuring the volume of gas evolved. The data gave the formulas NaH and KH. Moissan studied various properties of the hydrides. He found that they were insoluble in organic solvents, and that they reacted with carbon dioxide to form formates. The dissociation pressures were not measured.

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[1] *Recherches physico-chimiques*, 1, 176.

[2] *Compt. rend.*, 78, 807 (1874).

[3] *Ibid.*, 134, 71 (1902).

2. The Experimental Method.

The apparatus used to study the dissociation of the hydrides is represented in Fig. 1. The method followed was to distil the metals into the reaction tubes and then to connect them with the manometers without permitting contact with the air. The manometers being exhausted, hydrogen was admitted and the reaction tubes were heated, by means of a resistance furnace, to the desired temperature.

The metals used were taken from the same stock as was employed in in the electrode potential measurements of Lewis and Kraus[1] and Lewis and Keyes.[2]

The hydrogen was prepared *in vacuo* by the action of air free distilled water on 4% sodium amalgam. The apparatus for this purpose is represented by I (Fig. 1). The amalgam was placed in I and distilled water

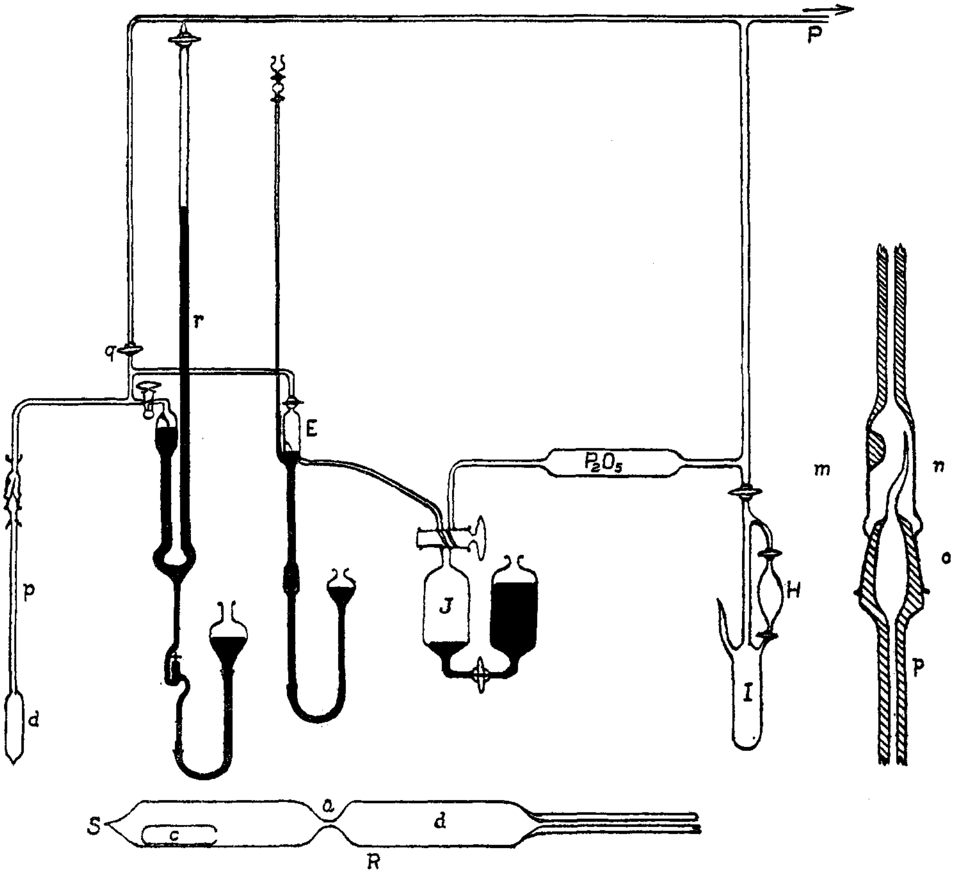

Fig. 1.

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[1] This Journal, 32, 1459 (1910).

[2] *Ibid.*, 34, 119 (1912).

in H. The apparatus, including the part J, was thoroughly exhausted through P. The stopcock at the upper end of the water chamber H was opened during the exhaustion for the purpose of boiling the water, thus freeing it completely from dissolved air. After exhaustion, a few drops of water were admitted to the amalgam and the whole apparatus re-exhausted. The water was then run onto the amalgam, and the evolved hydrogen, after being dried by means of the phosphorus pentoxide tube shown in the figure, was collected in the reservoir J.

The method of preparing the reaction tubes *d* was as follows: A small portion of metal was placed in the capsule *c*. The latter was then introduced into the reaction tube R and the end of the reaction tube sealed off at S. The capillary portion of the reaction tube was joined to the ground connection *p*. The tip of the latter was then sealed to the pump, and the whole reaction tube completely exhausted. By means of a cylindrical resistance heater which slipped over the tube R the metal could be distilled into the part of the tube marked *d*. The portion of the reaction tube containing the capsule could then be sealed off at *a* and the tip *n* sealed from the pump. Connection was then made with the manometers *r* by means of the ground glass piece *m*. After exhausting the manometer connections, the reaction tube *n* was rotated in the ground glass joint until the tip *n* pressed against the glass projection inside *m*, thus breaking off the tip and affording communication with the inside of the reaction tube. By this device the clean distilled metal could be introduced without contact with the air. Hydrogen was now admitted from the reservoir J, and the temperature of the furnace having been adjusted, the equilibrium pressures could be read off directly on the manometer *r*.

The furnace used was constructed of a 35 cm. length of iron pipe having an internal diameter of 15 cm. The pipe was covered with asbestos cloth and mica, and was wound with suitable resistance wire. A fan was introduced from the bottom of the furnace to provide vigorous stirring. As has been pointed out before, vigorous stirring is essential if a uniform temperature is desired. Temperatures were measured by means of a copper-constantan thermoelement. The temperature-electromotive force curve for the couple was obtained from the boiling points of water, naphthalene, benzophenone, and sulphur. The values for the boiling points under atmospheric pressure, together with the electromotive force values, are given in the following table:

	Boiling-point.	E. M. F. in millivolts.
Water	100.0	3.150
Naphthalene[1]	218.0	8.830
Benzophenone[1]	306.0	13.550
Sulphur	444.7	21.57

[1] *Bull. Bureau of Standards*, 7, 8 (1911).

The attempt was made to study the rate of the reaction at different temperatures. The measuring chamber E was used to introduce a measured volume of hydrogen; and from this and the known volume of the reaction tube the initial pressure could be computed. The rate was not proportional to the hydrogen pressure, owing probably to surface effects in the reaction bulb. The rate[1] of absorption of hydrogen, however, is approximately sixteen times as rapid at 300° as at 200°. Above 300° the rate of absorption of hydrogen was so rapid that accurate readings could not be obtained on the manometer.

Some difficulty was experienced above 375°–400°, owing to the action of the metal on the glass. The glass walls of the reaction tube were of course thoroughly heated before distilling in the metal. This precaution seemed to lessen the action very materially. In the case of sodium, the action was much more marked than in the case of potassium. The result of this action on the glass seemed to be the production of a gaseous product, since on lowering the temperature—say to 300°—the observed pressure was greatly in excess of the equilibrium pressure. On the other hand, in the case of experiments where a temperature of 380°–400° was not exceeded, the equilibrium pressures at the lower temperatures could be produced exactly. In fact, the equilibrium pressures were obtained with both increasing and decreasing temperature in every experiment. On account of the difficulty described above, no measurements were made much above 400°.

3. The Vapor Pressures of Liquid Sodium and Potassium.

The equilibrium pressure determined by the method described above is the sum of the partial pressures of the hydrogen in equilibrium with the metal, the vapor pressure of the solid metal hydride, and that of the metal. The equilibrium pressure of the hydrogen alone is needed to determin the constants in the equation which is to represent the results. The vapor pressure of the solid metal hydride was neglected. The vapor-pressures of the metals have been measured only in the case of sodium. Jewett[2] determined the vapor density of metallic sodium, and from the data obtained he computed the vapor pressure at the corresponding temperatures. Gebhardt[3] measured directly the vapor pressure of this metal between 380° and 570° in a glass apparatus. The two sets of data do not agree even approximately—Jewett giving 10.72 mm. at 410° and Gebhardt 1.7 mm. at the same temperature. In view of the action of the metal on glass referred to above, it is probable that even Gebhardt's

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[1] In $2^1/_4$ min. at 300° the pressure dropped from 575 mm. to 501 mm., while at 215° the pressure fell from 477.5 mm. to 418 mm. in 39 min.

[2] *Phil. Mag.*, 4, 546 (1902).

[3] *Ber. physik. Ges.*, 3, 184 (1905).

values are much too high. That there are in reality serious errors in Gebhardt's data is shown by the fact that they give values for the heat of evaporation of the metal which increases enormously with increasing temperature, whereas they should decrease.

A more reliable estimate of the vapor pressure may be obtained by means of the following computation based upon the vapor pressure equation of Clausius and on Trouton's rule, which states that the ratio of the molal heat of vaporization to the boiling point on the absolute scale is constant. Mercury has been found to give the value 22 for Trouton's constant. Assuming that this constant has the same value for sodium and potassium, and taking the boiling points of these metals as 878° and 758°, we obtain 25,322 cal. and 22,678 cal., respectively, for the atomic heats of evaporation (L). With the aid of these data, and of the difference (ΔC_p) of the atomic heat capacities of the liquid metal (as given by Bernini[1]) and of the monatomic vapor (as calculated from the kinetic theory), we may substitute numerical values in the following thermodynamic equation expressing the change of the vapor pressure p with the temperature T:

$$\log p = \int \frac{L_0 + (\Delta C_p)T}{RT^2} dT + \text{const.}$$

We thus obtain the equations:

$$\text{For Na:} \quad \log_{10}p = -\frac{6200}{T} - 1.35 \log_{10}T + 12.40.$$

$$\text{For K:} \quad \log_{10}p = -\frac{6000}{T} - 0.40 \log_{10}T - 0.0008T + 10.73.$$

These equations give for the vapor pressure of sodium at 400°, 0.24 mm., and for that of potassium, 1.4 mm. The magnitude of the vapor-pressure of the metals themselves may therefore be neglected, in comparison with the dissociation pressure of the hydrides.

4. The Equilibrium Pressures of Sodium Hydride.

A large number of reaction tubes were prepared in the manner already described. No effort was made to adjust the temperature for fixed intervals or at any particular point, but measurements were made at various temperatures between about 250° and 400°. The equilibrium pressures within this interval were obtainable for either rising or falling temperatures. The separate observations are given in Table I. The pressures are expressed in millimeters of mercury.

These data were combined by plotting the logarithm of the pressure in millimeters against the reciprocal of the absolute temperature. A

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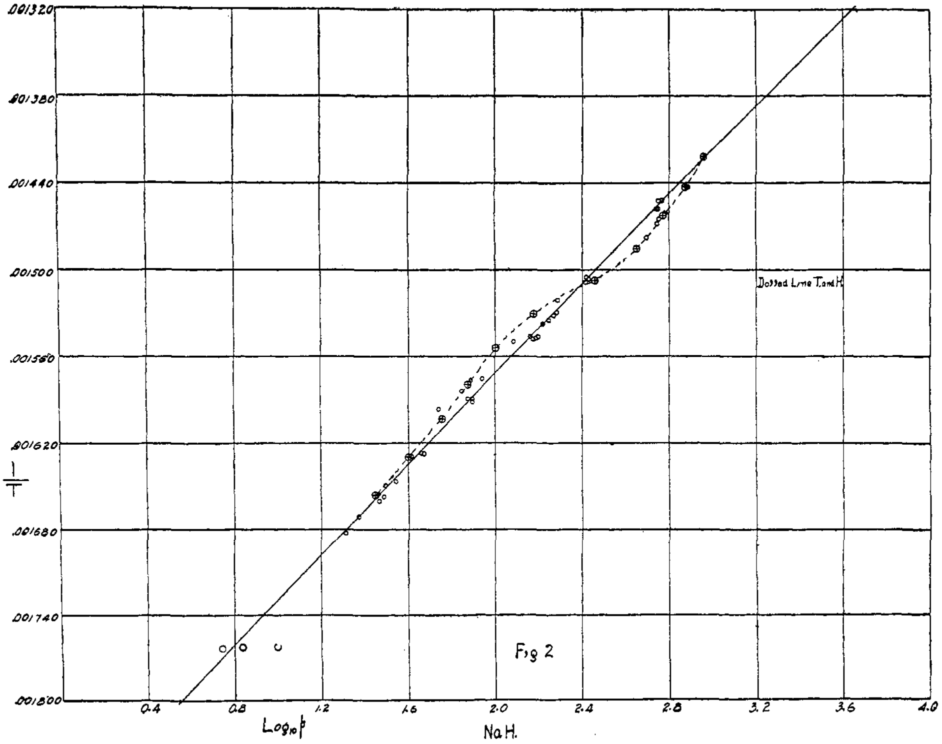
[1] *Physik. Z.*, 7, 168 (1906).

TABLE I.—OBSERVED VALUES OF THE VAPOR PRESSURE OF SODIUM HYDRIDE.

t.	p.	t.	p.	t.	p.	t.	p.
267.0°	1.5	334.6°	34.9	372.8°	152.9	406.5°	560.5
274.0	2.0	340.0	41.0	373.2	146.9	407.7	560.8
279.8	4.0	341.4	46.7	373.3	155.4	408.0	560.8
293.7	6.8	341.5	46.4	374.0	158.0	412.5	562.1
294.0	4.3	353.0	55.3	377.3	166.0	413.2	554.6
313.8	5.5	355.5	78.5	379.6	187.0	413.5	556.5
320.8	20.5	356.2	74.8	380.0	192.3	413.5	570.4
325.2	22.5	356.4	78.5	384.1	193.7	414.8	587.3
329.5	29.0	358.5	70.5	389.8	261.5	414.8	588.0
330.2	31.0	361.5	82.5	390.5	270.8	...	...
332.7	32.8	372.0	121.5	391.0	262.7	...	...

large scale plot like that represented in Fig. 2 was thus obtained. From this plot the pressures were read off at a series of round temperatures



differing by 10°, and the values so read off are given in Table II in the column headed "obs." The column headed "T and H" contains the data obtained by Troost and Hautefeuille.

TABLE II.—VAPOR PRESSURES OF SODIUM HYDRIDE AT ROUND TEMPERATURES.

t.	Obs. $\log_{10} p$.	Calc. $\log_{10} p$.	Obs. p.	T and H.	Calc. p.
290°	0.700	0.718	5.01	...	5.22
300	0.904	0.902	8.02	...	7.98
310	1.094	1.093	12.42	...	12.40
320	1.270	1.275	18.62	...	18.84
330	1.454	1.452	28.45	28.0	28.31
340	1.620	1.6234	41.69	40.0	41.98
350	1.792	1.7894	61.94	57.0	61.58
360	1.950	1.9574	89.13	75.0	90.66
370	2.110	2.1067	128.83	100.0	127.91
380	2.260	2.2586	181.97	150.0	181.39
390	2.410	2.4062	257.0	280.0	254.8
400	2.550	2.5496	354.8	447.0	354.5
410	2.694	2.6888	....	598.0	488.4
420	...	2.8244	....	752.0	667.4
430	...	2.9566	....	910.0	904.9

From these equilibrium pressures and existing data on specific heats, it is possible to evaluate the heat of dissociation and its change with the temperature. The heat of reaction was calculated for the two temperature intervals 340°–350° and 350°–360° by means of the equation

$$2.3 \log_{10} p_1/p_2 = Q_t/R(1/T_2 - 1/T_1);$$

and the average of these values, 14,740 cal., was taken to represent the heat of dissociation of one formula weight NaH at 350°. By combining this with the heat capacity data the change of the heat of the reaction with the temperature was obtained. The heat capacity of liquid sodium has been determined by Bernini,[1] and found to be 7.68 cal. per gram atom. The molal heat capacity of hydrogen was taken to be $6.5 + 0.0009\ T$. The atomic heat capacity of hydrogen in its compounds was taken as 2.3, and that of sodium as 6.4, giving 8.7 cal. for the heat capacity of NaH. From these data we obtain the equation $Q_T = 13110 + 2.5T$.

The heat of reaction at ordinary temperature is calculated to be 13,860 cal. per gram atom of sodium. Forcrand[2] measured the heat of this reaction by dissolving definit portions of NaH in water, and found the heat evolved to be 25,800 cal. per mol. of sodium hydride. The heat of solution of sodium was taken as 42,400 cal. per gram atom of sodium. The heat of formation of sodium hydride is accordingly 16600 cal. This value is considerably larger than that obtained from the equilibrium measurements. Forcrand made four experiments, using 0.0120, 0.0380, 0.0227 and 0.0070 gram of material. According to his value of the heat of reaction the largest quantity used would give to the calorimeter about 40.8 cal., while the smallest quantity would give approximately 7.5 cal.

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[1] *Loc. cit.*

[2] Forcrand, *Compt. rend.*, 140, 990 (1905).

What type of calorimeter Forcrand used is not stated. Neither does he mention the quantity of water used in the calorimeter. The quantity necessary to give one degree rise, assuming the calorimetric apparatus to have zero heat capacity, would be only 40.8 cc. in one case and 7 cc. in another.

By substituting the above expression for Q_T in the thermodynamic equation $d \log p = Qt/RT^2dT$ and integrating, we obtain the following expression for the dissociation pressure p of sodium hydride at any temperature:

$$\log_{10}p = -5700/T + 2.5 \log_{10}T + 3.956.$$

The values calculated by this equation are given in Table II in the column headed "calc." It will be seen that the deviations between the observed and calculated values seldom exceed 1%.

5. The Equilibrium Pressures of Potassium Hydride.

The observed values of the equilibrium pressures of potassium hydride are given in Table III.

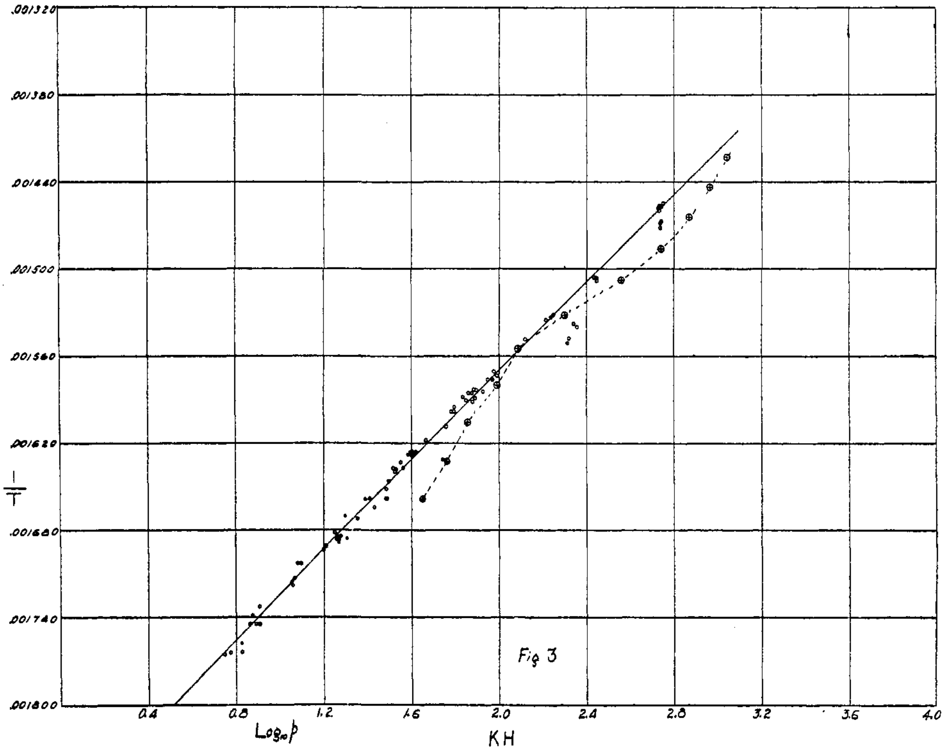
TABLE III.—OBSERVED VALUES OF THE VAPOR PRESSURES OF POTASSIUM HYDRIDE.

t.	*p.*	*t.*	*p.*	*t.*	*p.*	*t.*	*p.*
215.0°	0.1	319.5°	18.5	341.0°	39.8	377.3°	218.5
250.0	0.5	320.0	18.5	341.5	41.3	376.0	227.5
270.0	2.1	320.8	18.8	342.0	40.2	378.5	164.3
290.0	4.8	321.6	17.9	345.0	46.0	379.0	172.8
293.7	5.6	325.1	22.5	349.0	57.3	380.0	175.8
293.9	6.7	326.2	19.8	353.0	62.3	389.8	279.6
294.0	6.0	328.3	27.0	354.2	62.8	390.5	277.0
295.5	6.7	330.0	27.8	355.5	77.0	391.0	273.0
300.0	7.7	330.2	30.5	356.4	77.5	406.5	541.8
302.0	7.5	330.3	25.7	358.0	73.9	407.7	542.5
304.0	8.1	332.7	30.5	358.5	85.0	408.0	542.7
309.0	11.5	334.6	33.0	359.0	77.8	412.5	539.5
310.0	11.4	337.0	34.0	361.5	91.6	413.2	535.3
311.0	11.6	337.8	33.8	363.0	98.0	413.5	543.0
314.2	12.6	338.0	34.8	364.0	95.0	414.8	563.7
318.1	15.8	339.0	37.3	372.0	205.5	...	...
318.5	16.3	340.2	55.5	373.2	208.5	...	...

These values were treated according to the same procedure as that followed in the case of sodium hydride. The data were plotted with $\log p$ and $1/T$ as coördinates, as shown in Fig. 3. The equation obtained is:

$$\log_{10}p = -5850/T + 2.6 \log_{10}T + 3.895.$$

The heat of reaction per equivalent of potassium hydride is calculated to be 14,240 cal. at ordinary temperatures. No direct measurement of the heat of this reaction has been previously made. The observed vapor



pressure interpolated for round temperatures and the vapor pressures calculated by the above equation are presented for comparison in Table IV.

TABLE IV.—VAPOR PRESSURES OF POTASSIUM HYDRIDE AT ROUND TEMPERATURES.

t.	Obs. log p.	Calc. log. p.	Obs. p.	T. and H.	Calc. p.
300°	0.866	0.865	7.31	...	7.32
310	1.060	1.053	11.49	...	11.29
320	1.246	1.240	17.62	...	17.38
330	1.426	1.424	26.6	45.0	26.55
340	1.600	1.598	39.8	58.0	39.61
350	1.768	1.770	58.6	72.0	58.89
360	1.934	1.937	85.9	98.0	85.5
370	2.094	2.098	124.2	122.0	125.3
380	2.248	2.255	177.0	200.0	179.89
390	2.404	2.407	253.5	363.0	255.27
400	2.556	2.555	259.74	548.0	258.92
410	2.706	2.697	508.15	736.0	497.73
420	2.852	2.839	....	916.0	690.24
430	2.998	2.976	....	1114.0	946.24

6. Summary.

The dissociation pressures of sodium hydride and potassium hydride between 250° and 400° have been measured; and the following equations expressing them in millimeters of mercury have been derived:

$$\text{For NaH: } \log_{10}p = -5700/T + 2.5\log_{10}T + 3.956.$$

$$\text{For KH } \log_{10}p = -5850/T + 2.6\log_{10}T + 3.895.$$

The vapor pressure equations for liquid sodium and potassium have been calculated from the following data: (1) the boiling points of these substances; (2) their heats of vaporization, derived from Trouton's rule (assuming the same constant as for mercury); and (3) the heat capacities of the liquids and the vapor. These equations are

$$\text{For Na: } \log p = -6200/T - 1.35\log T + 12.4.$$

$$\text{For K: } \log p = -6000/T - 0.40\log T - 0.0008T + 10.73.$$

The heat of reaction at ordinary temperatures has been calculated from the measurements, and found to be 13,860 calories per formula-weight of sodium hydride (NaH) and 14,240 calories per formula-weight of potassium hydride (KH).

BOSTON, March. 1912.

A CORRELATION OF THE ELASTIC BEHAVIOR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.

BY JOHN JOHNSTON.

Received April 15, 1912.

As is well known, the effect of pressure acting on both the solid and liquid phase of a single substance is to raise or lower its melting point according as the process of melting is accompanied by an increase or a decrease of volume respectively, the latter being the exceptional case. But when pressure acts only on the solid phase, but not—or not to the same extent—on the liquid phase, the melting point is always lowered and by an amount which is many times as great as the corresponding change produced by the same pressure acting on both the liquid and the solid phase. For example, the melting point of ice is lowered by 0.0075° per atmosphere of equal pressure, but by about 12 times as much, or 0.09° per atmosphere, when the pressure acts only on the ice.[1] The latter type of pressure we shall for convenience in what follows designate by the term "unequal pressure."

A study of the work of Spring and others rendered evident a parallelism between the melting point of a substance and the ease with which it will, when subjected to (non-uniform) compression, flow or weld into a more or less solid block; namely, that the higher the melting point of the material, the less readily does it flow, or weld together, under compression.

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[1] Cf. J. H. Poynting, *Phil. Mag.*, [5] **12**, 32 (1881); Ostwald's "*Lehrbuch der Allgemeinen Chemie*," 2 Aufl., Vol. 2, II, pp. 374–9; or Roozeboom's "Heterogene Gleichgewichte," Vol. 1, pp. 213–7.