

term to convert from rational to molal activity coefficients. They were able to reproduce, quantitatively, the experimental activity coefficients in aqueous solution of a large number of electrolytes up to four and five molal. It is of interest to determine if the equation is valid for liquid ammonia

TABLE III

COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE WITH THOSE CALCULATED BY EQUATION OF STOKES AND ROBINSON

<i>m</i>	Parameters: $a = 3.53$ ; $n = 2.5$	
	$\gamma_{\text{expt.}}$	$\gamma_{\text{calcd.}}$
0.001	(0.780)	0.778
.002	.705	.706
.003	.655	.658
.005	.589	.588
.01	.480	.484
.02	.372	.377
.05	.242	.245
.10	.160	.164
.20	.104	.103
.30	.0767	.0775
.40	.0614	.0629
.50	.0540	.0535

solutions and, if so, to compare solvation in water and ammonia. The parameters were varied to obtain the best fit to the data for sodium chloride. The results are given in Table III. Good agreement was obtained for  $a = 3.53 \pm 0.02 \text{ \AA.}$ , and  $n = 2.5 \pm 0.2$  with an average difference between the calculated and observed coefficients of 4 in the third significant figure. Stokes and Robinson found for sodium chloride in water solution that  $a = 3.97 \text{ \AA.}$  and  $n = 3.5$ . This difference between the two solvents is reasonable in view of their dielectric constants.

The hydration parameter could not be determined for potassium chloride since the terms in the equation containing  $n$  are negligible at the highest concentration used. The parameter,  $a$ , was determined by fitting the data to the Debye-Hückel equation for uni-univalent electrolytes,  $\log \gamma = -A\sqrt{m}/(1 + aB\sqrt{m})$ , where  $A$  and  $B$  are constants equal to 3.5835 and 0.3922, respectively. A value for  $a$  of  $3.3 \pm 0.1 \text{ \AA.}$  reproduces the data to  $\pm 0.003$  in  $\gamma$ . A value of 3.63 was found by Stokes and Robinson for potassium chloride.

LAFAYETTE, IND.

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## Thermal Properties of the Alkali Metals. I. The Heats of Reaction of Sodium and Potassium with Water at 25°<sup>1,2</sup>

BY EUGENE E. KETCHEN AND W. E. WALLACE

The heats of reaction of potassium and sodium with an infinite quantity of water at 25° were measured and found to be  $-47,190 \pm 80$  and  $-44,350 \pm 70$  calories/gram atom, respectively. These results are in reasonably good agreement with other recent determinations except for Roth and Kaule's work on the sodium-water reaction.

### Introduction

While determining the heats of formation of sodium-potassium alloys reported in the following paper, it became necessary to have reliable values for the heats of reaction of the two pure metals with water. Since several earlier determinations of these heat effects led to somewhat divergent results,<sup>3,4</sup> particularly for potassium, it seemed desirable to carry out a redetermination of these important thermochemical quantities in the hope that more reliable values might emerge. The measured heat effects are of interest not only for their use in obtaining heats of alloying but also because much of the thermochemical information pertaining to sodium and potassium compounds depends on the determinations of the heat produced when the metals react with water.

### Experimental Methods

**Calorimeter.**—The calorimeter employed in this study was the instrument constructed for studying the heats associated

(1) From a thesis submitted to the University of Pittsburgh by Eugene E. Ketchen in partial fulfillment of the requirements for the Doctor of Philosophy degree, August, 1950.

(2) This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

(3) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(4) W. A. Roth and H. L. Kaule, *Z. anorg. Chem.*, **253**, 352 (1947).

with the formation of ionic solid solutions.<sup>5</sup> Constructional details and operating characteristics have been reported in connection with that work. The only modification needed in the present study was the replacement of the crushing devices used to introduce the salts into the calorimeter by a special chamber for carrying out the metal-water reaction.

The reaction chamber consisted essentially of a monel rod drilled out to receive the reactants and nickel plated on the interior to improve its corrosion resistance to the alkaline solution produced. Its operation will be made clear in the discussion which follows.

In a typical experiment approximately 0.002 to 0.006 gram atom of alkali metal contained in a crushable glass bulb was allowed to react with about 20 g. of water. From 90 to 270 calories of heat were developed, being communicated for the most part to water (about 1 kg.) surrounding the reaction chamber.

There are several sources of difficulty customarily associated with experiments of this type. These have presumably been eliminated in the reaction chamber used. Much of the trouble stems from the violence with which the reaction takes place. In such reactions the reactants are frequently blown apart before the process has gone to completion. To minimize this possibility a series of baffles was provided. Evidently these baffles were very effective in confining the reactants for the relatively short reaction time for if any alkali metal had been thrown up and lodged above the water level, reaction would have been continued with water vapor and this mishap would have been recognized by the thermal response of the calorimeter toward the conclusion of an experiment. With the chamber employed no such behavior was ever observed. In preliminary experiments using a chamber of a somewhat different design a slow

(5) M. A. Fineman and W. E. Wallace, *THIS JOURNAL*, **70**, 4165 (1948).

TABLE I  
HEATS OF REACTION OF SODIUM AND POTASSIUM WITH WATER AT 25°  
Reaction: Metal(s) + ∞H<sub>2</sub>O(l) = Metallic hydroxide(∞H<sub>2</sub>O) + 1/2H<sub>2</sub>(g)

Metal	Individual determinations, cal./g. atom	Mean value, cal./g. atom
Sodium	-43,940, -44,370, -44,530, -44,070, -44,800 -44,450, -44,400, -44,190	-44,350 ± 70
Potassium	-47,570, -47,320, -47,160, -47,120, -46,820 -47,150	-47,190 ± 80

heat-evolution, persisting after the main reaction, was frequently observed and was attributed to the reaction between water vapor and some alkali metal which had been blown out of contact with liquid water.

In previous investigations trouble seemed to have developed frequently from the interference of atmospheric oxygen or carbon dioxide at the time of or immediately following the reaction. If the alkali metal reaches the surface and oxygen is present, the hydrogen formed by the process is ignited and partially burned rendering the final state of the system indefinite. Carbon dioxide is also objectionable in that it reacts with the alkali formed to render the final state of the system again uncertain. With the present reaction chambers these sources of trouble were eliminated by having the space above the water level evacuated except for water vapor.

Another source of trouble arises when the hydrogen produced in the reaction is allowed to escape from the reaction chamber. Frequently heat is lost either by incomplete heat exchange of the escaping hydrogen or from the water evaporated. In the present work these effects were eliminated by having the reaction chambers completely enclosed and entirely submerged in the calorimeter. Thus no hydrogen or water escaped from the reaction chamber during the experiment.

**Materials.**—The sodium used was purchased from the Fisher Scientific Company. It was stated to be the best grade available commercially. Spectroscopic examination indicated that only calcium was present in anything but traces. Upon colorimetric analysis the calcium content was established to be less than 0.04%. Consequently this material was used without further purification.

Through the courtesy of Dr. C. B. Jackson of the Mine Safety Appliances Company of Callery, Pa., a large quantity of very pure potassium, prepared by fractional distillation, was made available for the present study. Spectroscopic examination of this material showed it to contain no more than 0.01% of sodium and to be free of other metals except for traces. This metal was also used without further purification.

**Handling of Samples.**—For the experiments it was necessary to free the metals of their oxide coating and then remove a small sample from the stock supply to be sealed off in a glass bulb for weighing and storing prior to use in the calorimeter. The oxide coating was cut away with a knife as well as could be done in the open and a large chunk of metal so prepared was transferred to a specially designed dry-box.<sup>6</sup> Initially attempts were made to finish cleaning up the stock supply and divide it into samples of suitable size in a high vacuum system which was provided with the necessary remote control devices to carry out manipulations inside the vacuum system. Later all the necessary operations were carried out in the dry-box under an atmosphere of helium which had been purified by liquefaction.

The alkali metals after being placed in the dry-box were melted so as to allow the residual oxides to come to the surface. Samples of suitable size were pipetted from beneath the surface of the molten metals into sample bulbs which were then sealed off as described previously.<sup>6</sup> The samples so obtained had bright mirror-like surfaces. To test the effectiveness of the procedure used in handling the samples the masses of several sodium samples were established both by weighing and by titrating the alkali formed using a weight buret. The results agreed in all cases to better than 0.1%.

## Results

Numerous experiments were performed before the techniques for handling the extremely reactive

(6) Eugene E. Ketchen, Forrest A. Trumbore, W. E. Wallace and R. S. Craig, *Rev. Sci. Instruments*, **20**, 524 (1949).

TABLE II  
COMPARISON OF VARIOUS DETERMINATIONS OF THE HEATS OF REACTION OF SODIUM AND POTASSIUM WITH WATER

Reaction: Metal(s) + ∞H <sub>2</sub> O = metallic hydroxide(∞H <sub>2</sub> O) + 1/2H <sub>2</sub> (g)		-ΔH
Investigation	Date	cal./g. atom of metal
Sodium		
Thomsen <sup>a</sup>	1880	43,920 ± 200
Joannes <sup>a</sup>	1887	43,440 ± 200
Rengade <sup>a</sup>	1908	44,360 ± 230
Hagen and Seiverts <sup>a</sup>	1929	44,780 ± 210
Roth and Kaule <sup>b</sup>	1947	45,380 ± 150
This research	1950	44,350 ± 70
Potassium		
Thomsen <sup>a</sup>	1880	48,460 ± 300
Joannes <sup>a</sup>	1887	46,190 ± 280
Rengade <sup>a</sup>	1908	46,780 ± 150
This research	1950	47,190 ± 80

<sup>a</sup> See footnote 3. <sup>b</sup> See footnote 4.

alkali metals in preparing samples and in the calorimeter were satisfactorily worked out. These preliminary results have been disregarded. The final measurements consisted of a series of eight determinations of the heat of reaction of sodium and water and six determinations of the corresponding heat effect for potassium. The results are shown in Table I where corrections to infinite dilution have been made using Sturtevant's data for sodium hydroxide<sup>7</sup> and Harned and Cook's data for potassium hydroxide.<sup>8</sup> The uncertainties listed are the probable errors of the mean computed from the expression  $p = 0.6745 \sqrt{\frac{\sum \delta^2}{n(n-1)}}$

where  $p$  is the probable error of the mean,  $\delta$  is the deviation of an individual observation from the mean and  $n$  is the number of observations.

**Comparison with Results Obtained in Other Investigations.**—The several investigations leading to determinations of the heats of reaction of sodium and potassium with water at 25° are listed in Table II together with the mean values taken from Table I. Of the studies mentioned Roth and Kaule's determinations for sodium are the only recent ones in substantial disagreement with the results obtained in this research. Roth and Kaule's high value for the heat of reaction of sodium with water may have resulted from one of the difficulties mentioned earlier in this paper, namely, the failure to confine the reactants at the time of the reaction. In their experiments the sodium-water reaction took place under a submerged funnel. The funnel ended in a glass spiral, also submerged in water, through which the hydrogen produced in the

(7) J. M. Sturtevant, *THIS JOURNAL*, **62**, 2276 (1940).

(8) H. S. Harned and M. S. Cook, *ibid.*, **59**, 496 (1937).

reaction made its escape from the calorimeter. In preliminary experiments a device similar in principle to that used by Roth and Kaule was employed in the present study and high results frequently occurred. In those early experiments the quantity of alkali metal participating in the reaction was ascertained by titrating the alkali produced. Later when the technique was perfected for estimating the mass of the sample also by weighing, it was noted that in such experiments the masses by titration were consistently lower than masses by weighing presumably due to a loss of alkali at the instant of the reaction.<sup>9</sup> The high

(9) When carried out in the open, the reaction of the alkali metals with water always produces a white smoke which is probably some oxide or hydroxide volatilized by the intense heat of the reaction.

heat of reaction obtained in the preliminary experiments would therefore appear to be due in part to an incorrect account for the mass of alkali metal taking part in the reaction.<sup>10</sup> Since Roth and Kaule determined the amount of reaction by titrating the alkali formed, it may be that their high value was due to a similar error. This assumes, of course, that the quantity of alkali missing at the time of the titration had at least partially reacted and transmitted some heat of reaction to the calorimeter.

(10) Very likely in these early experiments some of the hydrogen ignited. This would, of course, also contribute to a high value for the heat evolved.

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## Thermal Properties of the Alkali Metals. II. The Heats of Formation of Some Sodium-Potassium Alloys at 25<sup>o</sup><sub>1,2</sub>

BY EUGENE E. KETCHEN AND W. E. WALLACE

The heats of formation of several sodium-potassium alloys are presented. These data are based upon the measured heats of reaction of the alloys and the two pure metals with water. Heat effects are reported for the alloying of the solid metals and the undercooled liquids. The latter data are compared with results to be expected from Hildebrand's theory of regular solutions and the quasi-chemical theory. Substantial disagreement between experiment and both theories is evident. The disagreement can be explained qualitatively by assuming the exothermal formation of the previously observed intermetallic compound Na<sub>2</sub>K.

### Introduction

The heat effect accompanying the formation of an alloy is a quantity of considerable interest. This kind of information is useful not only because of its bearing upon the chemical and physical behavior of alloys but also because it is intimately related to the character of the bonding in metallic systems. Whereas a complete theory of the metallic bond would permit an exact calculation of the heat of alloying, there is as yet no theory capable of providing even a crude estimate of these quantities. This situation exists not only for metallic systems but for other systems as well. It has been shown elsewhere<sup>3</sup> that even in the simple case of ionic solid solutions involving only the comparatively well understood electrostatic bond, in systems characterized by unusual structural simplicity, the small energy changes associated with the formation of the solutions cannot be accounted for satisfactorily in terms of existing theories.

Under these circumstances it is clear that reliable measurements of the heats associated with alloy formation are useful in at least two respects—first, for use in studying alloys from the conventional point of view of chemical thermodynamics and second, by their existence to encourage theoretical work on this interesting aspect of the theory of metals. Such data can be of considerable

use as a sensitive appraisal of future theoretical work along these lines.

The success of theory in accounting for the properties of the alkali metals is well known.<sup>4</sup> This suggests that if a successful theory can be developed to account for heats of alloying, very likely it will be worked out for the alkali metal alloys. For that reason the investigation of the thermochemistry of sodium-potassium alloys reported in this paper was undertaken.

The principle employed in the present study has frequently been used in obtaining heats of alloying.<sup>5</sup> It consists of measuring the difference in heat produced when first the alloy and then the pure metals react with a suitable reagent. If care is taken that the final state is the same in both cases,<sup>6</sup> then the heat of alloying is the measured difference in heat effect. In the present work the heats of alloying were determined from the measured heats of reaction of alloys with water together with the heats of reaction of the pure metals with water given in the preceding paper.<sup>7</sup>

### Experimental Methods

**Calorimeter.**—The calorimeter employed and procedure followed have been described in the preceding paper.<sup>7</sup>

**Materials.**—The alloys used were supplied by Dr. C. B. Jackson of the Mine Safety Appliances Company of Cal-

(4) F. Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(5) F. Webke and O. Kubaschewski, "Thermochemie der Legierungen," Julius Springer, Berlin, 1943.

(6) Strictly speaking the final states need not be identical if their heat contents are equal.

(7) Eugene E. Ketchen and W. E. Wallace, *THIS JOURNAL*, **73**, 5810 (1951).

(1) From a thesis submitted to the University of Pittsburgh by Eugene E. Ketchen in partial fulfillment of the requirements for the Doctor of Philosophy degree, August, 1950.

(2) This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

(3) W. E. Wallace, *J. Chem. Phys.*, **17**, 1095 (1949).