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.[9] The high 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.[10] 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.

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[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.

[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°[1,2]

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_2K.

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[3] 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.[4] 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.[5] 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,[6] 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.[7]

Experimental Methods

Calorimeter.—The calorimeter employed and procedure followed have been described in the preceding paper.[7]

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

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[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).

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

[5] F. Weibke 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).

lery, Pennsylvania. They were prepared by fractional distillation of a large batch of sodium–potassium alloy. Spectroscopic examination showed these materials to be free of metallic contaminants except in traces. Their brilliant mirror-like surfaces made it seem rather unlikely that any non-metallic impurity was present.

Analyses.—By titrating the alkali formed when a known weight of sample reacts with water the composition of alloy can be determined. In such procedures precise titrations are essential. In this study all titrations were made using weight burets. At first the alkali was recovered from the calorimeter for the titration. In time this proved to be inconvenient and unsatisfactory mainly due to the difficulty of washing the intricate reaction chamber free of alkali.[7] Hence a simpler chamber was built for carrying out the analyses. This chamber possessed an additional advantage in that larger samples could be used and better analytical precision attained.

The reaction chamber used in the analyses functioned essentially the same as the calorimeter reaction chamber. The space above the water was evacuated and the reaction carried out in an enclosed system to prevent the loss of materials at the time of the reaction. When carried out in the open, the reaction of alkali metals with water always produces a white smoke which may be oxide or hydroxide volatilized by the intense heat of the reaction.

The effectiveness of the analytical procedure was tested by processing samples of pure sodium just as if they were an alloy. The "composition" of the sodium as shown by determinations performed in duplicate was 100.00 ± 0.03%.

Experimental Results

The measured heats of reaction are given in Table I. It is to be noted that the uncertainties[8] listed in conjunction with the quantities in column 3 include contributions from both the calorimetric and analytical determinations. Errors in analysis affect the uncertainties listed through their influence on the mass per gram atom of alloy.

TABLE I

HEATS OF REACTION OF SODIUM–POTASSIUM ALLOYS WITH WATER AT 25°

Reaction: Alloy (1) + ∞H_2O = mixed hydroxides (∞H_2O) + $^1/_2H_2$ (g)

Composition, potassium, atomic per cent.	No. of determinations	$-\Delta H$ cal./g. atom
37.41 ± 0.06	5	45,910 ± 70
48.46 ± .10	6	46,550 ± 80
62.10 ± .07	4	47,260 ± 100
68.16 ± .14	3	47,390 ± 40
78.14 ± .29	3	47,370 ± 60

Corrections to infinite dilution have been made assuming the heats of dilution of the mixed alkalies are additively related to the heats of dilution of the pure alkalies. Ordinarily this would be a questionable procedure.

However, in the present case the corrections to infinite dilution are small (approximately 100 cal./gram atom) and since the heats of dilution of the individual alkalies are virtually identical over the composition range involved,[9,10] it seems unlikely that a significant error could have entered from this source.

The heats of formation of the various alloys mentioned in Table I can be calculated from the heat effects listed therein provided the heats of reaction of the pure metals with water are known. The several determinations for the pure metals are listed in the preceding paper.[7] For consistency only the values obtained in this Laboratory were considered in calculating the heats of alloying.

$$(1)\quad \mathrm{Na(s)} + \infty \mathrm{H_2O(l)} = \mathrm{NaOH}(\infty \mathrm{H_2O}) + {}^1/_2\mathrm{H_2(g)} \qquad \Delta H = -44{,}350 \text{ cal.}$$

$$\mathrm{K(s)} + \infty \mathrm{H_2O(l)} = \mathrm{KOH}(\infty \mathrm{H_2O}) + {}^1/_2\mathrm{H_2(g)} \qquad \Delta H = -47{,}190 \text{ cal.}$$

The calculated results are shown in column 2, Table II.

TABLE II

HEATS OF FORMATION OF SODIUM–POTASSIUM ALLOYS AT 25°

Reaction: xNa + yK = $Na_xK_y(l)$; $x + y = 1$ g. atom

Atomic per cent. potassium	Heat of formation of alloy, cal./g. atom Solid reactants	Liquid reactants
37.41	500 ± 90	−60
48.46	820 ± 90	260
62.10	1150 ± 120	590
68.16	1100 ± 60	550
78.14	800 ± 80	230

It is also of interest to know the heats of formation of the alloys from the metals in the liquid state. These quantities, the heats of mixing of the liquid metals, are useful for comparison with theoretical attempts intended to account for the heats of mixing of liquids as discussed in the next section.

The heats of alloying from the undercooled liquids shown in column 3, Table II, were obtained from the data in column 2 with the aid of the recent investigations of the heat contents of sodium[11] and potassium[12] and their alloys[12] by Ginnings, Douglas and Ball. From tabulated values of the heat contents (relative to 0°) of the several materials it was possible to calculate heats of mixing of the molten metals at 100°. Douglas, Ball and Ginnings observed that for the temperature interval extending from 100 to 800° the heat capacities of the alloys are to within a per cent. additively related to those of the pure metals. This means, of course, that ΔC_p for the mixing of the molten metals is virtually zero and the heats of mixing are practically invariant with temperature. Thus, with negligible error the heats of mixing of the metals at 100° are the same as for the undercooled liquids at 25° provided the additivity relationship is assumed to hold between 25 and 100°.

Discussion of Results

Comparison with Other Work.—When the present study was begun, the only recent[13] determinations of the heats of formation of sodium–potassium alloys were those due to Kawakami.[14] He measured the heat effects associated with the direct mixing of the molten metals at 110°. After the series of measurements summarized in Table I were concluded, it was learned that McKisson and Bromley had just completed a number of

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(8) The uncertainties listed are probable errors. They have been computed by the formula given in the preceding paper.[7]

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

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

(11) D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).

(12) Private communication from Dr. Thomas B. Douglas.

(13) The early work of Joannis (*Ann. chim. phys.*, **12**, 358 (1887)) led to values of +980, +70, −650 and −290 cal./gram atom for the heat of formation of the alloys having compositions Na_2K, NaK, NaK_2 and NaK_3, respectively, at 180°. The values were derived from the heats of reaction of the pure metals and the alloys with water. Joannis' calorimetric precision was so low that his values appear to be without significance.

(14) M. Kawakami, *Sci. Rep. Tohoku Imp. Univ.*, **16**, 915 (1927).

experiments along the same lines as Kawakami. Their data have recently been published.[15] It is thus possible to compare the heats of mixing of liquid sodium and potassium obtained in three independent studies. The agreement (see Table III) is not impressive, even when the uncertainties of the several measurements are considered—approximately ± 100 cal. in the present work and somewhat less in the other cases.

TABLE III

HEATS OF MIXING OF SODIUM AND POTASSIUM AT 100°

	ΔH, cal./gram atom Na_2K	NaK	NaK_2
Kawakami	30	50	40
McKisson and Bromley	180	190	180
Authors	−100 (extrap.)	310	580

From the intercomparison of results shown in Table III several points emerge. First, the directly determined heats of mixing appear to be somewhat more trustworthy than those based on heat of solution measurements. Second, the latter results are probably not capable of being further refined. The limiting factor lies in the inherently uncontrollable character of the metal–water reaction. Third, the heat of mixing can undoubtedly be refined considerably (McKisson and Bromley indicate their data to be of a preliminary nature) to obtain heats of mixing for this system to a high degree of precision. Fourth, the spread between heats of alloying determined directly and indirectly is larger than the scattering would have in itself suggested. This point is particularly pertinent when it is realized that in studying the energetics of alloying in the solid state, the indirect method is frequently the only course of procedure available.[5]

Comparison of the Results Obtained in This Study with Theory.—There appear to be only two theoretical developments appropriate to consider in connection with the heats of alloying measured in this study—Hildebrand's theory of regular solutions and the so-called quasi-chemical theory due mainly to Guggenheim and Rushbrooke.[16] The heats of mixing of the liquid metals given in Table II were examined from the point of view of both treatments.

Calculations based on Hildebrand's equations show an endothermal heat of mixing with a maximum heat absorption of about one kcal./g. atom of alloy around 40 atomic per cent. potassium. In this region the experimental values obtained in the present study are nearly zero or perhaps slightly negative.[17] An intermetallic compound Na_2K has been reported to exist,[18] at least at low temperatures, and this casts considerable doubt on the relevance of Hildebrand's treatment to the present situation. It is of interest to point out, however, that for compositions above 65 atomic per cent. potassium the agreement between computed and observed results is within the limits of experimental error. Thus, the trend of the heats of mixing can be accounted for qualitatively by regarding the heat effects as originating in two ways, one due to internal pressure differences as considered in the Hildebrand treatment and leading to positive heat effects at all compositions and the other due to exothermal compound formation. For all compositions other than those immediately adjacent to that corresponding to the composition of the compound the former effect would be expected to predominate.

The heats of mixing were also examined from the point of view of the quasi-chemical theory. This theory is able to predict only the form of the energy of mixing–composition curve. To obtain actual values a single energy parameter must be evaluated from the experimental data. The quasi-chemical theory leads[16] to a heat of mixing curve symmetrical about mole fraction 0.5. Without presenting numbers it is obvious (see Table III) that the quasi-chemical theory also fails to account for the observed heats of mixing. The directly determined heats of mixing conform much more closely to the requirements of theory in that they appear to be nearly symmetrical about mole fraction 0.5.

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[15] R. L. McKisson and L. A. Bromley, THIS JOURNAL, **73**, 314 1951).

[16] For a general discussion of both of these theories see J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 119–154.

[17] ΔH_p is the measured quantity whereas ΔE_v is the quantity which should be compared with theory. The difference between ΔH_p and ΔE_v is within the error of ΔH_p so that the two quantities have been used interchangeably.

[18] E. Rinck, *Compt. rend.*, **197**, 49 (1933).