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HEATS OF FORMATION OF SODIUM POTASSIUM ALLOYS

Raleigh L. McKisson and LeRoy A. Bromley

April 17, 1950

Berkeley, California

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HEATS OF FORMATION OF SODIUM POTASSIUM ALLOYS

Raleigh L. McKisson and LeRoy A. Bromley

April 17, 1950

Abstract

Measurements of the heat of formation of sodium potassium alloys have been carried out by mixing liquid metals and noting the temperature drop.

The values found for the heats of formation from the elements in their standard states are: (The elements are solid at 25°C and liquid at 110°C)

NaK (l)	$\Delta H_{25°C} = +1430$	$\Delta H_{110°C} = +360$
NaK_2 (l)	$\Delta H_{25°C} = +2130$	$\Delta H_{110°C} = +530$
Na_2K (l)	$\Delta H_{25°C} = +2140$	$\Delta H_{110°C} = +530$

All values are accurate to about 100 cal/mole. None of the values agree well with previous workers.

HEATS OF FORMATION OF SODIUM POTASSIUM ALLOYS

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Introduction

Joannis[1] has measured the heats of formation of the sodium potassium alloys by the difference of the heats of solution of the alloys and the elements in water. Bichowski and Rossini[2] have corrected these values by using more accurate data on the heat of solution of the elements. Because of the very large heats evolved by this method, and since the desired heat is the difference of these very large quantities, it is not surprising that these values are in serious error.

Kawakami[3] has measured the heats of formation by noting the temperature change upon direct mixing of the elements in a calorimeter. Although details of the procedure are lacking it may be assumed that, since the quantities of materials used were rather small and since only a stream of hydrogen was used to prevent oxidation, some oxidation probably occurred. This would tend to lead to uncertainty in the results and would ordinarily be expected to give heats of formation which are too negative. (Too small positively)

Method and Procedure and Results

The method of direct addition of sodium to potassium was chosen as an inert atmosphere "dry box" was available. This facilitated handling large quantities of molten sodium and/or potassium. The argon atmosphere in the dry box was maintained oxygen and water free by an absolutely clean molten sodium surface over which the argon atmosphere was continuously blown except during actual experiments. The quantities of sodium or potassium used per addition in the measurements varied from one to 3 gram mols total. Tempera-

tures were measured with a mercury in glass thermometer graduated in degrees.

The first series of measurements were carried out by pouring hot liquid sodium into hot liquid potassium in a molybdenum container and measuring the resultant temperature. The known heat capacity of molybdenum was used to correct the results.

Since the effective heat capacity of the molybdenum crucible is somewhat in doubt, the results have a rather high uncertainty. The second series of runs were all made in a 1/2 pint small-neck dewar whose effective heat capacity was found by puring various amounts of hot NaK_2 into cool NaK_2 and noting the temperature change. This was repeated at two levels of melt and a linear heat capacity versus volume of melt was calculated. For the remaining runs the two separate materials to be mixed were heated to the desired temperature and one added to the dewar and the temperatures of the dewar checked until a slow rate of fall was noted. The temperature of the material to be added was then checked with the same thermometer. This material was then added quickly and stirred vigorously with the thermometer. The equilibrium temperature was attained in about 15 seconds. As a check on the temperature change on mixing two samples of NaK_2 at the same temperature one in the dewar and one to be added were mixed. This resulted in a drop of one °C (run 3, Table 1). Other runs were therefore corrected for this effect.

Typical runs are summarized in Table 1. Although for the sake of brevity the data are not complete, they show conclusively the magnitude of the heat effects when various ratios of sodium and potassium are mixed.

Discussion

On the basis of six runs similar to runs 1 and 2 (Table 1), the heat of formation of NaK was calculated. There appears to be a slight increase of ΔH

Table 1

Measured Data on Sodium-Potassium Alloys.

Run No.	Calorimeter Contents		Material Added		Final Melt		Heat of formation at average temp. cal./gm. mole of final composition.
	Temp. °C	Comp.	Temp. °C	Comp.	Temp. °C	Comp.	
1	117	Na	117	K	98	NaK	+ 400
2	223	Na	210	K	192	NaK	+ 440
3	135	NaK_2	135	NaK_2	134	NaK_2	0 chosen
4	107	NaK	135	Na	106	Na_2K	+ 200
5	130	NaK	156	K	130	NaK_2	+ 170
6	111	NaK_2	111	Na_2K	110	NaK	+ 60

with temperature. The heat of formation of Na_2K was calculated from three determinations similar to run 4, and the heat of formation of NaK_2 was calculated from three measurements similar to run 5.

The following reaction heat measured in two runs like No. 6 serve as a check on the results.

$$1/3\ Na_2K\ (l) + 1/3\ NaK_2\ (l) \rightarrow NaK\ (l)$$

$$\Delta H \text{ calculated} = +\ 20 \text{ cal.}$$

$$\Delta H \text{ measured} = +\ 70 \text{ cal.}$$

This is a reasonable check.

For this reason and from the very nature of the measurements it is felt that the final results are accurate to about ±100 cal. per gram mole.

It is of interest to estimate the heat to be expected if no compound formation were to occur. If one were to assume that sodium and potassium form a regular solution(4), then the heat of formation of NaK(l) from Na(l) and K(l) would be +2.0 kcal per gram mole. Since the measured heat, although positive is considerably more negative than this, this indicates a tendency for compound formation which indeed shows up in the phase diagram as the peritectic melting compound Na_2K.

Summary

The heats of formation of three compositions of sodium potassium alloys have been measured and are listed in Table 2. The results were obtained by measuring the direct heat effect upon mixing the elements. The results differ rather seriously from those reported by other workers but it is felt that although high precision is not claimed in our work our results are not subject to large errors present in their results.

This work was performed under the auspices of the Atomic Energy Commission.

Table 2

Values for the Heats of Formation of Sodium-Potassium Alloys.

Worker	Temperature	ΔH in kilocalories/gm mole of composition shown		
		Composition		
		Na_2K	NaK	NaK_2
Authors	25°C	+ 2.14 ± 0.1	+1.43 ± 0.1	+2.13 ± 0.1
	110°C	+ 0.53 ± 0.1	+0.36 ± 0.1	+0.53 ± 0.1
Joannis[1]	18°C	+ 2.93	+0.14	-1.94
Bichowski and Rossini[2]	18°C	-0.4	-2.1	-5.3
Kawakami[3]	110°C	+0.10	+0.09	+0.11

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