energy changes. It may be mentioned, however, that with systems such as silica–alcohols, or cellulose–nitrogen, where the possibility of chemical reaction is much smaller, exactly the same type of $\Delta\gamma - p/p_0$ curves have been obtained.

Summary

1. Isoteric heats of adsorption of three aliphatic amines by silica gel were determined by means of adsorption isotherms obtained at 25° and at 40°.

2. The change in the heat content $\overline{\Delta H}$, the free energy $\overline{\Delta F}$ and the entropy $\overline{\Delta S}$ per mole of adsorbate were determined.

3. The isosteric heats and $-\overline{\Delta S}$ obtained for the initial stages of adsorption were so high as to indicate that adsorption in this range is not strictly physical.

4. From energy and entropy considerations it appears that at high relative pressures (*i. e.*, over the range represented by the hysteresis portions of the isotherms) condensation of vapor occurs within the capillaries.

5. From the Gibbs equation interrelating surface area, surface tension, surface excess and chemical potential, it becomes possible, with adsorption data alone, to determine the free surface energy change which occurs when unit area of solid (adsorbent) is wetted by a liquid. By definition this energy change represents the adhesion tension value of the system. The method for the determination of adhesion tension is particularly suited for use with porous solids.

6. Further evidence was obtained to substantiate the view that the surface tension of liquids in capillaries as small as exist in silica gel have practically the same values as when in bulk.

7. Through adsorption studies it is possible to determine the areas of the adsorbed liquid layers and also the thickness of the adsorbed liquid layer.

ANN ARBOR, MICHIGAN RECEIVED MAY 24, 1950

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Heats of Formation of Sodium Potassium Alloys[1]

BY RALEIGH L. MCKISSON AND LEROY A. BROMLEY

Introduction

Joannis[2] has measured heats of formation of the sodium potassium alloys by the difference of the heats of solution of the alloys and the elements in water. Bichowsky and Rossini[3] have corrected these values by using more accurate data on the heat of solution of the elements. Kawakami[4] has measured the heats of formation by noting the temperature change upon direct mixing of the elements in a calorimeter. The results of these authors are in such disagreement (see Table II) that further investigation is imperative. The results of the preliminary experiments in this Laboratory are reported herein.

Method, Procedure and Results

The method of direct addition of reactants was chosen because an inert atmosphere "dry box" which facilitated handling of large quantities of molten metals was available. The argon atmosphere in the dry box was maintained oxygen and water free by a clean molten sodium surface over which the argon atmosphere was continuously blown except during actual experiments. The quantities of sodium or potassium used in the measurements varied from two to three moles total. All temperatures were measured with the same mercury in glass thermometer graduated in degrees.

The procedure consisted of recording the temperature of the reactant in the calorimeter vessel when it attained a constant value, reading the temperature of the addendum with the same thermometer, and finally reading the temperature of the mixture after stirring vigorously with the thermometer. The equilibrium temperature was attained in about 15 seconds.

The calorimeter used for the NaK measurements consisted of a thin-walled molybdenum container. Heat capacities were calculated using the data of Kelley[5] and the total weight of molybdenum. A 0.5 pint dewar was used as the calorimeter for the Na_2K and the NaK_2 measurements. Its effective heat capacity was measured by the method of mixtures at two melt heights and a linear relation between heat capacity and melt height was assumed. Corrections were made for the temperature drop in the addendum during pouring, and for the temperature drop of the dewar while equilibrium was attained. The former correction was about −3°, the latter, −1°.

Determinations were made at a number of different temperatures for the alloy NaK so that a value for ΔC_p of the reaction could be obtained. The least squares method was used to fit a straight line to the experimental points. The reaction is

$$\mathrm{Na(l)} + \mathrm{K(l)} \longrightarrow \mathrm{NaK(l)}$$

The equation, in cal./mole and °K., is

$$\Delta H_f = 42 + 0.86\ T$$

The determinations on the alloys NaK_2 and Na_2K were made using NaK and adding the required element. Heat effects were measured and combined with the ΔH_{f298} of NaK, and the C_p data of Kelley[5] to evaluate ΔH_{f298} for the products. Table I shows the values of ΔH_{f298} found in the various runs.

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(1) Based on University of California Radiation Laboratory Report UCRL 671, April 17, 1950.

(2) Joannis, *Ann. Chim. Phys.*, [6] **12**, 358 (1887).

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

(4) M. Kawakami, *Tohoku Imperial University Science Reports*, Series I, **16**, 915 (1927).

(5) K. K. Kelley, U. S. Bureau of Mines, Bulletin No. 476 (1949)

TABLE I

SUMMARY OF DATA ON LIQUID SODIUM POTASSIUM ALLOYS

Run	Product	ΔH_{f298},[a] cal./mole	Run	Product	ΔH_{f298},[a] cal./mole
3	NaK	+1500	8	Na_2K	+2030
4	NaK	+1390	9	Na_2K	+2180
5	NaK	+1490	10	Na_2K	+2170
6	NaK	+1470	11	NaK_2	+2150
7	NaK	+1410	14	NaK_2	+2120
13	NaK[b]	+1380	16	NaK_2	+2130

[a] From solid elements yielding liquid alloy. [b] Dewar flask used for calorimeter.

Discussion

The average ΔH_{f298} for the alloys measured are given in Table II. Internal consistency of these results was verified by runs 12 and 15 which measured the reaction

$$Na_2K(l) + NaK_2(l) \longrightarrow 3NaK(l)$$

The measured heats for this reaction was +59 and +60 cal., respectively. The value calculated by combination of the ΔH_{f298} in Table II is $+60 \pm 240$ cal. Although the close agreement is undoubtedly accidental, the consistency is obvious.

The average deviations of the NaK, Na_2K and NaK_2 results are ±50 cal., ±60 cal. and ±10 cal., respectively, when calculated from the data of Table I. However, since the Na_2K and NaK_2 results are dependent upon the NaK result, an arbitrary assignment of ±100 cal. seems in order.

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,[6] then the heat of formation of NaK(l) from Na(l) and K(l) would be +2000 cal./mole. Since the measured heat is smaller $\sim(+300)$, it indicates a tendency for association which indeed is evidenced in the phase diagram as the peritectic melting compound Na_2K.

TABLE II

VALUES FOR ΔH_f OF LIQUID SODIUM–POTASSIUM ALLOYS[a]
ΔH IN CAL./MOLE OF COMPOSITION SHOWN

Worker	Temp., °C.	Composition and ΔH_f		
		Na_2K	NaK	NaK_2
Authors	25	$+2130 \pm 100$	$+1440 \pm 100$	$+2130 \pm 100$
	110	$+540 \pm 100$	$+370 \pm 100$	$+540 \pm 100$
Joannis[1]	18	+2930	+140	−1940
Bichowsky and Rossini[2]	18	−400	−2100	−5300
Kawakami[3]	110	+100	+90	+110

[a] The elements are solid at 25° and liquid at 110°.

Summary

The heats of formation of three compositions of sodium potassium alloys have been measured and are listed in Table II. 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 our results are not subject to large errors.

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

(6) J. H. Hildebrand, "Solubility of Non-Electrolytes," A.C.S. Monograph, 1936.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

The Vapor Phase Dissociation of Some Carboxylic Acids. I. Acetic Acid[1,2,3,4]

BY MODDIE D. TAYLOR

Sometime ago an interest developed to study the vapor phase dissociation of some substituted carboxylic acids with the view to determine how it is affected by certain substituents.[5] It was decided to use acetic acid, whose dissociation has been studied most often, to standardize the technique. Examination of the literature revealed that the heat of dissociation values reported for acetic acid vary from 13.8 to 16.4 kcal.[6] These measurements have been made over a wide range of pressures and temperatures. Johnson and Nash[5] worked over the pressure range of 160 to 1150 mm. and a corresponding temperature range of 80 to 200°. Ritter and Simons[7] worked over the pressure range of 45 to 813 mm. and a corresponding temperature range of 50 to 210°. MacDougall[8] worked over the pressure range of 5 to 25 mm. and a corresponding temperature range of 25 to 40°. Fenton and Garner[9] worked over the pressure range of 120 to 290 mm. and a corresponding temperature range of 185 to 230°. Nernst and von Wartenberg[10] worked over the pressure range of 400 to 1500 mm. and a corresponding temperature range of 40 to 200°.

Dissociation studies of acetic acid conducted at pressures as high as the ones listed above do not yield thermodynamic constants when the simple gas and equilibrium laws are applied due to the deviation of the gas from ideal behavior. Ritter and Simons[6] and Johnson and Nash[5] found it necessary to postulate higher polymers of acetic acid than the dimer in order to interpret their data successfully. They attempted to obtain thermodynamic values of dissociation constants and heat of dissociation with an extrapolation procedure. MacDougall worked in an ideal pressure range but his temperature range was such that

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(2) Sincere appreciation is expressed to Lincoln University (Mo.) where this work was begun and whose sympathetic coöperation and support made its beginning possible.

(3) Presented before the Washington Section of the American Chemical Society, October, 1950.

(4) For a table supplementary to this article order Document 2910 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting 0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or 0.50 for photocopies (6 × 8 inches) readable without optical aid.

(5) This phase of the problem is now being investigated.

(6) E. W. Johnson and L. K. Nash, THIS JOURNAL, **72**, 547 (1950).

(7) H. L. Ritter and J. H. Simons, *ibid.*, **67**, 757 (1945).

(8) F. H. MacDougall, *ibid.*, **58**, 2585 (1936).

(9) F. M. Fenton and W. E. Garner, *J. Chem. Soc.*, 694 (1930).

(10) Nernst and von Wartenberg, *Z. Elektrochem.*, **22**, 37 (1916).