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.

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 ± 100	+1440 ± 100	+2130 ± 100
	110	+ 540 ± 100	+ 370 ± 100	+ 540 ± 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°.

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 ± 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 ~(+300), it indicates a tendency for association which indeed is evidenced 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 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.

BERKELEY 4, CALIF.

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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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(1) Supported, in part, by Grant No. 907, Penrose Fund, American Philosophical Society.

(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).

only a small dissociation range was covered which lay in the vicinity of larger probable error. It would seem that a careful study in a low pressure range over a sufficiently large temperature range to encompass the whole range of dissociation of acetic acid would offer a satisfactory method for obtaining the true thermodynamic constants. Such a study has been made.

Experimental

Apparatus.—Final purification, transfer and storage of materials were achieved in an all glass vacuum system closed with mercury Stock valves. Dissociation pressures were measured in a dissociation tensimeter especially designed for the accurate measurement of low pressures and first used by the author in collaboration with Dr. H. C. Brown.[11] The tensimeter was calibrated by filling it with pure, dry hydrogen chloride at a known temperature and pressure, completely removing the acid by condensation with liquid nitrogen and titrating it with standard barium hydroxide. At a pressure of 95 mm. and a temperature of 30° at which the tensimeter was filled, hydrogen chloride is assumed to be a perfect gas. This method yielded a value of 359.8 ml. for the volume of the dissociation tensimeter. Pressures were measured to 0.01 mm. with a Gaertner micrometer slide (range 100 mm.) carrying a short focus telescope. Temperatures were measured to 0.1° with total immersion, 50° range, Anschütz thermometers, calibrated by the National Bureau of Standards with no deviation greater than 0.2°. Temperatures were maintained constant by a variable electrically heated oil thermostat of the type which has been previously described.[11]

Purification of Acetic Acid.—Baker Co. reagent grade acetic acid was purified by the method of Eichelberger and LaMer[12] which consisted of refluxing it for 10 hours with a small amount of chromium trioxide, distilling, refluxing with triacetyl borate and distilling away. A second method of purification consisted of one distillation through a two-foot Vigreux column and subsequent fractional freezing in an apparatus of the type described by Ritter and Simons[7] which was so designed that a portion of the acid could be disposed of without exposing the desired fraction to the atmosphere. The freezing point remained constant after two fractional freezings. Samples of acid purified by both methods exhibited the accepted freezing point (16.6°) of acetic acid. Another constant for pure acetic acid (believed reported here for the first time) is its vapor pressure at the triple point. If a sample of the completely frozen acid is permitted to warm up to room temperature, its vapor pressure slowly rises to the value 9.5 mm. and remains constant until the acid is more than half melted. All samples of acid were finally fractionated in the vacuum line and a middle fraction used.

Method of Analysis.—Carbonate-free 0.05 *N* barium hydroxide which had been standardized against constant boiling hydrochloric acid was used as the assaying reagent and phenol red as the indicator. For the purpose of analysis, samples of acetic acid were condensed into tared sample take-off tubes (which had been attached to the line by means of plicene cement) by cooling with iced water. The tube was sealed-off the line, the residual part removed and freed from plicene and the final weight taken. The sample tube was constructed with a curled capillary tail which could be broken under carbon dioxide free water so as to remove the acid quantitatively and permit its titration. After a bit of experience, this method of analysis proved quite successful. Analyses of the acetic acid samples by this procedure, which is believed to be accurate to 0.2%, showed them to be 99.8% pure.

Procedure of Measurement.—A sample of acetic acid, sufficiently small to exist completely in the vapor phase, was condensed into the dissociation tensimeter and its pressure, at constant volume, measured every 10° over the temperature range of 50 to 150°. The sample was permitted to cool partially and then opened to a sample take-off tube, cooled in a carbon dioxide–ether-bath for fifteen minutes and then sealed off the line. Analysis was performed in the manner already described. Corrections were made for the variation of the density of mercury with temperature. Variation of the volume of the dissociation tensimeter with temperature was insignificant.

Methods of Calculation

A knowledge of the mass, temperature and volume of the acid permits the calculation of its pressure assuming no dissociation and ideal behavior according to the formula

$$P_i = (760\,gTR)/(120.1PV) \qquad (1)$$

Likewise, formula (1) can be used to calculate P_o, the pressure which the undissociated gas would exhibit at 0°. Assuming that the acid dissociates in conformity with the equation

$$(\mathrm{HOAc})_2 = 2\mathrm{HOAc} \qquad (2)$$

the degree of dissociation is given by

$$\alpha = (P/P_i) - 1 \qquad (3)$$

and the equilibrium constant is given by

$$K = 4\alpha^2 P/(1 - \alpha^2) \qquad (4)$$

Substituting equation (2) in (3) one obtains

$$K = 4(P - P_i)^2/(2P_i - P) \qquad (5)$$

which is more useful for certain calculations. The heat of reaction is calculated graphically making use of the van't Hoff equation

$$\mathrm{d}(\log k)/\mathrm{d}(1/T) = -\Delta H/2.303R \qquad (6)$$

Results and Discussion

In this investigation eight dissociation studies of acetic acid were performed covering the range of 10 to 90% dissociation. Complete data for study,[8] a typical one, are summarized in Table I and Fig. 1. Condensed data for studies 1 to 7 are summarized in Table II.[13]

TABLE I

SUMMARY OF DISSOCIATION STUDY OF ACETIC ACID[a]

t, °C.	P (mm.)	P_i (mm.)	α	K (mm.)
51.2	25.98	22.00	0.1809	3.52
60.6	28.22	22.63	.2470	7.33
71.3	31.31	23.36	.3403	16.4
81.3	34.35	24.04	.4289	31.0
91.0	37.48	24.70	.5174	54.8
100.6	40.68	25.33	.6060	94.4
111.3	44.30	26.07	.6993	170
121.1	47.35	26.74	.7707	270
131.1	50.09	27.42	.8268	433
140.5	52.54	28.05	.8731	674
150.5	54.91	28.73	.9112	1075

[a] Ml. of 0.0568 *N* $Ba(OH)_2$ = 13.80; P_0 = 1852.

TABLE II

CONDENSED SUMMARY OF DISSOCIATION STUDIES 1 TO 8

Study	P_0 (mm.)	ΔH(cal.)	Equilibrium constants (mm.), log K =
1	21.90	15,250	$-3332/T + 10.897$
2	34.23	15,380	$-3361/T + 10.977$
3	13.15	15,180	....
4	14.06	15,350	....
5	17.93	15,320	$-3349/T + 10.918$
6	27.90	15,070	....
7	30.54	15,370	$-3359/T + 10.971$

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(11) Brown, Taylor and Gerstein, THIS JOURNAL, **66**, 432 (1944).

(12) W. C. Eichelberger and V. K. LaMer, *ibid.*, **55**, 3633 (1933).

(13) Complete data are available as an A. D. I. Document, see Footnote (4).

The analyses for studies 3, 4 and 6 were unsuccessful, but inasmuch as the pressures had been very carefully measured, it was felt that they could still contribute to the heat of dissociation value. The P_0 values for these samples were computed by making use of an equilibrium constant which had been calculated from the equation

$$\log K = -3347/T + 10.931 \qquad (7)$$

which is an average equation based on studies 1, 2, 5, 7 and 8. Equilibrium constants from studies 3, 4 and 6 have not been used in the computation of precision measures.

Equations for studies 1, 2, 5, 7 and 8 have been used to calculate equilibrium constants at the temperatures 80, 100 and 120°. The mean for the five values at the respective temperatures along with their respective probable errors are: 28.6 ± 0.7, 92.0 ± 0.8 and 262 ± 0.7%. The relative probable errors associated with the means appear to be nearly independent of the magnitude of the equilibrium constant. This relative error is believed to be associated with the equilibrium constants calculated with equation (7). The mean value of ΔH computed from all the studies is 15,270 calories with 70 calories being the probable error of a single value.

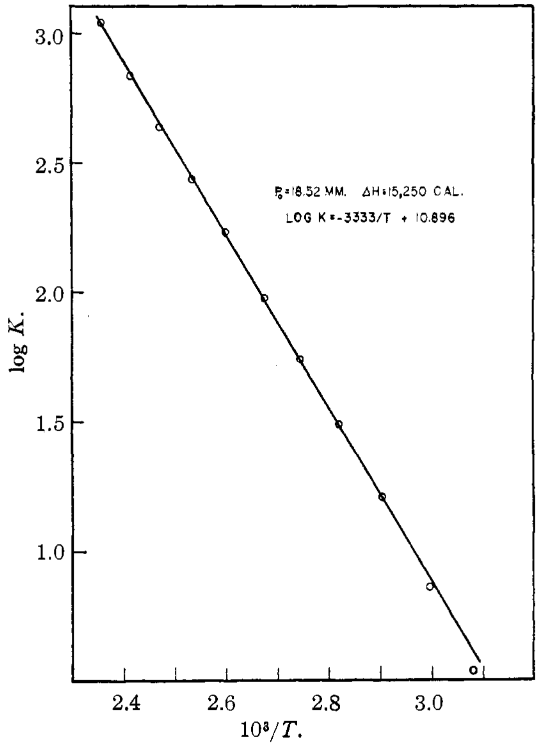

Fig. 1.—Summary of dissociation study—VIII.

Summary

The vapor phase dissociation of acetic acid has been studied over the pressure range (for dimer calculated to 0°) of 13 to 34 mm. and the temperature range of 50 to 150°. Data have been obtained from eight studies. The linearity of the middle portion of all the graphs suggests that dimer formation is the only phenomena occurring in this pressure range and that the value obtained for ΔH is the thermodynamic heat of dissociation. A heat of dissociation of 15,270 ± 100 cal. with a probability greater than 90% has been computed. An equation, $\log K = -3347/T + 10.931$, which is believed to express equilibrium constants to ±1.0% with a probability of 65% has been derived. The free energy of dissociation and the entropy of dissociation at 100° are computed to be 1,570 cal. and 36.7 cal./deg., respectively. At the triple point acetic acid exhibits a vapor pressure of 9.5 mm. Other values of the heat of dissociation of acetic acid which have been determined by vapor phase studies are 16.4,[8] 14.5,[9] 15.0,[10] 14.5[7] and 13.8[6] kcal.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF OBERLIN COLLEGE]

Synthesis of Some 2-Methoxy-8-keto-4a-methylperhydrophenanthrenes

BY W. B. RENFROW, ANTOINETTE RENFROW, ELLEN SHOUN AND C. A. SEARS

The stereoisomeric 2-methoxy-8-keto-4a-methylperhydrophenanthrenes (IV) are of interest as possible intermediates in the synthesis of steroids.[1]

Our synthesis involves a modification and extension of the method of Bardhan and Sengupta[2] and of Kon[3] for the synthesis of octahydrophenanthrenes.

We prepared 2-carboethoxy-4-methoxy-2-[2-(*o*-anisyl)-ethyl]-cyclohexanone (Ia) by alkylation of 2-carboethoxy-4-methoxycyclohexanone with 2-(*o*-anisyl)-ethyl bromide. Compounds like Ia do not undergo ketonic cleavage in satisfactory yield when heated with alkali,[2,3,4] but can be converted to ketones by indirect methods.[3,4] Methanolysis[5] of Ia to a substituted pimelic ester occurred readily and the pimelic ester was recyclized by removing methanol[6] to form the sodio derivative of 2-carbomethoxy-4-methoxy-6-[2-(*o*-anisyl)-ethyl]-cyclohexanone. The latter compound corresponds to a β-ketoester with one α-hydrogen atom and mild alkaline hydrolysis produced 4-methoxy-2-[2-(*o*-anisyl)-ethyl]-cyclohexanone (Ib) in satisfactory yield.

The ketone (Ib) was converted to 1-methyl-4-methoxy-2-[2-(*o*-anisyl)-ethyl]-cyclohexanol (II) with methylmagnesium iodide.

The method previously employed[2,3] for cyclizing 2-(2-phenylethyl)-cyclohexanols by distillation

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[1] Synthesis of a 2-hydroxy-8-keto-4a-methylperhydrophenanthrene by a different method has been reported by Cornforth and Robinson, *J. Chem. Soc.*, 676 (1946).

[2] Bardhan and Sengupta, *ibid.*, 2520 (1932).

[3] Kon, *ibid.*, 1081 (1933).

[4] Hibbit and Linstead, *ibid.*, 470 (1936).

[5] The alcoholysis of β-ketoesters has been studied by Kutz and Adkins, THIS JOURNAL, **52**, 4391 (1930).

[6] McElvain, *ibid.*, **51**, 3124 (1929).