Further understanding of the greater solvation energy of ions in ammonia has been obtained from an approximate calculation of the solvation energy of gas ion pairs in this solvent. Following the general procedure employed by Eley and Evans[10] and Eley and Pepper,[11] it has been possible to account for the ammoniation energy of the alkali halide and calcium iodide gas ion pairs from electrostatic considerations alone, thereby removing any requirements of partial covalent bond character as part of the interaction.

In comparing the nature of the solvated electron with other large ions in ammonia, Ogg[12] has called attention to the small solvation energy of the electron by a comparison of the heats of the reactions

$$\mathrm{Na^+(g) + I^-(g) = Na^+(am) + I^-(am)}$$
$$\mathrm{Na^+(g) + e^-(g) = Na^+(am) + e^-(am)}$$

from which the solvation energy difference may be obtained for the expression

$$\mathrm{I^-(g) - e^-(g) = I^-(am) - e^-(am)}$$

From the appropriate thermochemical data[2,5,8,13] for each alkali metal and its iodide, and the corresponding calcium systems, we have calculated the differences in solvation energy of the gas ion pair and have presented the results in Table IV. Strictly speaking, the energy of unpairing of the solvated electron pair is required to make the calculated values correct and meaningful in an absolute sense. However, since it is an additive constant for each case, it may be omitted for use of the results in a relative manner. On the assumption of two-electron ionization of calcium in ammonia, we observe that good agreement is exhibited among sodium, potassium and calcium systems for the solvation energy differences of the iodide ion and the electron which confirms our earlier conclusion. The low value obtained for lithium solutions probably arises from an uncertainty in the thermochemistry of LiI since previous studies[2] have shown that lithium metal solutions are entirely comparable with the other alkali metal solutions.

TABLE IV

DIFFERENCE IN AMMONIATION ENERGY OF I^-(g) AND e^-(g)

Systems	$-\Delta H$, kcal./equivalent
LiI and Li	20.8
NaI and Na	31.5
KI and K	31.4
CaI_2 and Ca	32.8

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Entropy of Ionization of Protonic Solvents

BY WILLIAM L. JOLLY

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The heat of ionization of anhydrous acetic acid has been found to be $\Delta H° = 5700$ cal./mole. Combining this heat with the known ionization constant, one calculates an entropy of ionization, $\Delta S° = -38.6$ cal./deg. mole. This entropy of ionization, like the corresponding values for liquid ammonia, methanol and ethanol, is much more negative than the entropy of ionization of water.

Studies of ionic entropies in methanol[1] and ammonia[2] have led to the suggestion that ionic entropies in water are abnormally high. The entropies of ionization of water, ammonia, methanol and ethanol are in agreement with this hypothesis. Table I gives the thermodynamic constants for the self-ionization of these solvents. It is apparent that the entropy of ionization of water is much more positive than that for the other three solvents. An explanation may be given in terms of entropies of solvation and the high degree of hydrogen bonding in water. When an ion enters water, more disorder is created than when it enters another, less hydrogen bonded, solvent.

The present work was carried out to determine whether acetic acid, an acidic solvent, parallels other non-aqueous solvents by having an entropy of ionization much more negative than that of water.

The free energy of ionization of anhydrous acetic acid has been measured by various investigators, and so in order to determine the entropy of ionization, it was necessary to merely determine the heat of ionization. This was accomplished by indirectly measuring the heat of neutralization of a strong acid (perchloric acid) and a strong base (sodium acetate) in anhydrous acetic acid. Two heats were determined, corresponding to the reactions

$$\mathrm{NaOAc\ (s) = Na^+\ (HOAc) + OAc^-\ (HOAc)}$$
$$\mathrm{NaOAc\ (s) + H^+\ (HOAc) = Na^+\ (HOAc) + HOAc\ (HOAc)}$$

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[1] W. M. Latimer and C. M. Slansky, THIS JOURNAL, **62**, 2019 (1940).

[2] W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952).

TABLE I

THERMODYNAMIC CONSTANTS FOR SELF-IONIZATION AT 25°

Solvent	$-\log K$	ΔH°, cal./mole	ΔS°, cal./deg. mole
H_2O	14.00[3]	13,360[3]	−19.2[3]
NH_3	29.8[5]	26,200[4]	−49
CH_3OH	16.6[6]	11,200[7]	−38.6
C_2H_5OH	18.9[8]	11,500[9]	−48.0

The difference between the heats of these two reactions is the heat of neutralization sought.

It should be mentioned that the calculations depend on the assumption that NaOAc, $NaClO_4$ and $HClO_4$ are completely dissociated in acetic acid. This assumption is justified on the basis of the conductance measurements of Kolthoff and Willman.[10]

Experimental

1. **Apparatus.**—A glass calorimeter of 1100-ml. capacity was used in all the runs. The sodium acetate samples were contained in small glass tubes attached with wax to the lower end of the stirring shaft. Introduction of the sample was accomplished by thrusting a glass rod through the bulb. The details of the calorimeter are described elsewhere.[11,12] All heats were measured at 25.0 ± 1.0° and are expressed in terms of the defined calorie.[13]

2. **Materials. NaOAc.**—Two preparations of sodium acetate were used; they shall be referred to as preparations A and B.

Reagent grade $NaOAc \cdot 3H_2O$ was recrystallized from a dilute solution of acetic acid in water and partially dried by keeping in a vacuum desiccator for two weeks. The material was finally dried by heating in an oven overnight at 100° (preparation A).

Reagent grade $NaOAc \cdot 3H_2O$ was recrystallized from glacial acetic acid and partially dried by keeping in a vacuum desiccator over sodium hydroxide for two days. The material was finally dried by heating in an oven at 130° for four hours (preparation B).

Preparation A was not analyzed. By titration in anhydrous acetic acid with a standard perchloric acid solution (using tropeolin 00 as indicator), preparation B analyzed 101 ± 1% pure. The precision of the titrations was about ±1%. By distillation of a mixture of phosphoric acid and preparation B, followed by titration of the distillate with standard base, preparation B analyzed 99.1 ± 0.5% pure.

Acetic Acid.—The melting point of reagent grade glacial acetic acid was determined and the acid was then refluxed with the appropriate amount of acetic anhydride to eliminate all the water, assuming water to be the only initial impurity. Samples of acetic acid used in the various calorimetric runs had melting points no lower than 16.48°, indicating a water content less than 0.07%. (The true melting point of acetic acid is 16.61°.)[13]

Perchloric Acid Solutions.—A known volume of 11.22 molar perchloric acid was added to an equal volume of anhydrous acetic acid. The mixture was chilled and enough acetic anhydride to react with the water present was slowly added. The mixture was then allowed to stand at room temperature for several hours and was finally diluted to the desired concentration with anhydrous acetic acid. The concentration of perchloric acid was checked by titrating with a standard acetate solution (prepared by dissolving a known amount of primary standard sodium carbonate in acetic acid).

Results and Conclusions

It was decided to check the heat of solution of anhydrous sodium acetate in water, so three runs were carried out in order to measure this quantity. The experimental details are given in Table II. Inasmuch as the dilutions were so great, the extrapolation to infinite dilution shall be neglected; hence $\Delta H^\circ = -4.1$ kcal./mole for NaOAc(s) = $Na^+(\infty aq) + OAc^-(\infty aq)$. This is to be compared with the value −4.3 kcal./mole given by the National Bureau of Standards[13] and the value −4.08 kcal./mole (at 18°) given by Bichowsky and Rossini.[14]

TABLE II

THE HEAT OF SOLUTION OF SODIUM ACETATE IN WATER

Run	NaOAc, g.	H_2O, g.	ΔH, kcal./mole
1	0.4306 (A)	1070	−4.08
6	.5656 (A)	1072	−4.00
7	.7201 (B)	1064	−4.24

Table III gives the details of four determinations of the heat of solution of sodium acetate in acetic acid. Run 3 was carried out using the same acid plus 0.5997 g. of NaOAc used in run 2; run 9 was carried out using the same acid plus 0.6443 g. of NaOAc used in run 8. The average value, $\Delta H^\circ = -4.8$ kcal./mole, is taken for NaOAc(s) = $Na^+(HOAc) + OAc^-(HOAc)$.

TABLE III

THE HEAT OF SOLUTION OF SODIUM ACETATE IN ACETIC ACID

Run	NaOAc, g.	HOAc, g.	ΔH, kcal./mole
2	0.5997 (A)	1129	−4.70
3	.9264 (A)	1129	−4.70
8	.6443 (B)	1051	−4.91
9	.5963 (B)	1051	−4.93

Table IV gives the details of four determinations of the heat of solution of sodium acetate in acetic acid solutions of perchloric acid. Run 5 was carried out using the same solution plus 0.8689 g. of NaOAc used in run 4. The value $\Delta H^\circ = -10.5$ kcal./mole is taken for NaOAc(s) + H^+(HOAc) = HOAc(HOAc) + Na^+(HOAc). Hence

TABLE IV

THE HEAT OF SOLUTION OF SODIUM ACETATE IN ACETIC ACID SOLUTIONS OF PERCHLORIC ACID

Run	NaOAc, g.	$HClO_4$ soln., g.	Molarity $HClO_4$	ΔH, kcal./mole
4	0.8689 (A)	1096	0.376	−10.53
5	.7243 (A)	1096	.366	−10.52
10	.6523 (B)	1055	.248	−10.69
11	.5475 (B)	1117	.539	−10.38

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(4) H. D. Mulder and F. C. Schmidt, *ibid.*, **73**, 5575 (1951).

(5) This value is calculated from the free energy of formation of amide ion given in the addendum to reference 2.

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$\Delta H^\circ = 5.7$ kcal./mole for HOAc(HOAc) = $\mathrm{H^+}$(HOAc) + $\mathrm{OAc^-}$(HOAc), the ionization of anhydrous acetic acid.

Kolthoff and Willman[10] reported the ionization constant of anhydrous acetic acid to be 2.5×10^{-13} at 25°, and Kilpi and Puranen[15] reported 2.8×10^{-13}. Kolthoff and Willman note in their paper that e.m.f. measurements of Hall[16] and Hall and Conant[17] lead to a value of about 10^{-10} for the ionization constant. It should be pointed out that Hall and Conant worked with solutions of rather high ionic strength and with acetic acid which may have contained as much as 0.5% water (0.28 molal in H_2O). An average value, $K = 2.6 \times 10^{-13}$, is taken for the ionization constant on a volume basis at 25°. Taking the density of acetic acid as 1.044 at 25°,[18] this is corrected to $K = 2.4 \times 10^{-13} =$ $(\mathrm{H^+})(\mathrm{OAc^-})$ on a molality basis, corresponding to a free energy of ionization of 17,210 cal./mole. Combining this with the heat of ionization, 5,700 cal./mole, one obtains $\Delta S^\circ = -38.6$ cal./deg. mole. This entropy is much more negative than the corresponding value for water, and bears out the conclusion that ionic entropies in water are higher than those of other protonic solvents.

Recent work by Smith and Elliott[19] indicates that perchloric acid is far from completely ionized in acetic acid. It may be necessary to re-interpret the results of the present investigation in light of these new findings.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND METALLURGY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY]

Thermodynamic Properties of Indium(III) Oxide[1]

BY MORRIS F. STUBBS, JOSEPH A. SCHUFLE AND ALVIN J. THOMPSON

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The free energy and enthalpy change for the formation at 298°K. of In_2O_3 have been determined to be −196.4 and −216.8 kcal./mole, respectively, by equilibrium methods. The absolute entropy of the oxide is then calculated to be 30.1 e.u./mole. X-Ray evidence indicates the reduction of In_2O_3 with hydrogen probably takes place directly to the metal with no appreciable amounts of lower oxides being formed under the conditions studied (823–1123°K.).

This work was undertaken to determine the standard free energy and enthalpy of formation of indium oxide by thermodynamic methods. The method used was to determine the equilibrium ratios of water vapor to hydrogen in the reduction of indium(III) oxide with hydrogen over the temperature range 823–1123°K.

The enthalpy of formation of indium oxide was first determined by Ditte[2] from the heats of solution of indium and indium oxide in sulfuric acid. Ditte's value of −240 kcal./mole was used by Latimer[3] to estimate the free energy of formation of the oxide as −218 kcal./mole. Becker and Roth[4] determined the enthalpy of formation of the oxide by combustion of the metal and obtained a value of −222.5 ± 0.7 kcal./mole. These authors also estimated the entropy of the oxide to be 27.0 ± 2.5 e.u./mole. Hart,[5] in a recent survey of the periodicity of chemical thermodynamic functions, used the Becker and Roth value for the enthalpy of formation, and gave −73.5 e.u./mole for entropy of formation, and calculated a value of −200.5 kcal./mole for free energy of formation. Recently, a new value for the enthalpy of formation of In_2O_3 has been determined by Holley, Huber and Meierkord[6] by the combustion of indium metal in an oxygen bomb calorimeter. They report finding a value of −221.27 ± 0.40 kcal./mole.

Experimental

Material, Apparatus and Procedure.—The In_2O_3 was prepared from 99.96% indium. The pure metal was dissolved in hydrochloric acid and the excess acid evaporated off on a hot-plate. The resulting $InCl_3$ was dissolved in water and hydrous indium oxide precipitated from the solution with 6 *F* ammonium hydroxide. The hydrous oxide was washed thoroughly and ignited to constant weight at 800°.

It was first necessary to establish the mechanism of the reduction of In_2O_3 with H_2. A charge of pure In_2O_3 was slowly reduced in a stream of H_2 at 600° in a porcelain boat placed in a Vycor tube in an electric furnace. Samples were removed from the boat at intervals for analysis and X-ray examination. The results obtained show only two crystalline forms, those of In_2O_3 and In metal. The reduction, therefore, probably takes place under the conditions described according to the reaction represented by the equation: $In_2O_3(s) + 3H_2(g) \rightleftarrows 2In(l) + 3H_2O(g)$ and not through the intermediate formation of InO and In_2O, as reported by Thiel and Luckmann.[7] (There is a possibility, of course, that in cooling the sample from the furnace temperature to room temperature, InO and In_2O could disproportionate to In and In_2O_3.)

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