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ABSTRACT

The heat of ionization of anhydrous acetic acid has been found to be $\Delta H^o =$ 5,700 cal./mole. Combining this heat with the known ionization constant, one calculates an entropy of ionization, $\Delta S^o = -38.6$ cal./deg. mole. This entropy of ionization, like the corresponding value for liquid ammonia, is much more negative than the entropy of ionization of water.

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Studies of ionic entropies in methanol[1] and ammonia have led

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[1] W. M. Latimer and C. M. Slansky, J. Am. Chem. Soc. 62, 2019 (1940).

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to the suggestion[2] that ionic entropies in water are abnormally high.

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[2] W. L. Jolly, "Heats, Free Energies and Entropies in Liquid Ammonia,"

UCRL-1402, June 15, 1951.

An explanation of this hypothesis 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 entropies of ionization of ammonia and water are in agreement

with the same idea. For ammonia, $\Delta S^{\circ} = -49$[3]; for water, $\Delta S^{\circ} = -19.2$[4].

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[3]Using the heat of ionization recently determined by H. D. Mulder and

F. C. Schmidt, J. Am. Chem. Soc. **73**, 5575-7 (1951).

[4]K. S. Pitzer, J. Am. Chem. Soc. **59**, 2365 (1937).

The present work on acetic acid shows that the entropy of ionization

of acetic acid is also very negative, and helps extend this idea.

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 following reactions:

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

$$NaOAc(s) + H^{+}(HOAc) = Na^{+}(HOAc) + HOAc(HOAc).$$
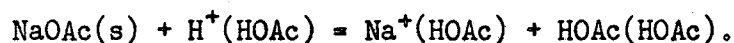
The difference between the heats of these two reactions is the heat

of neutralization sought.

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 bulbs 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[5,6]. All heats were measured at 25.0° ± 1.0°C. and are

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[5]B. J. Fontana, National Nuclear Energy Series, IV-19B, McGraw-Hill,
New York, 1950, p. 321.

[6]W. M. Latimer and H. W. Zimmerman, J. Am. Chem. Soc. 61, 1550 (1939).

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expressed in terms of the defined calorie[7]

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[7]National Bureau of Standards, Selected Values of Chemical Thermodynamic
Properties, Washington, D. C.

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2. Materials.--

NaOAc: Two preparations of sodium acetate were used; they shall be
referred to as preparations A and B.

Reagent grade NaOAc·3H$_2$O was recrystallized from a dilute solu-
tion 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°C. (Preparation A).

Reagent grade NaOAc·3H$_2$O 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°C. for four hours. (Preparation B).

Preparation A was not analyzed. By titration in anhydrous acetic
acid with a standard perchloric acid solution (using tropeolin OO as

indicator), preparation B analyzed 101 ± 1% pure. The precision of
the titrations was about ±1%. By distillation of a mixture of phos-
phoric acid and preparation B, followed by titration of the distillate
with standard base, preparation B analyzed 99.1 ± .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°C.,
indicating a water content less than .07%. (The true melting point
of acetic acid is 16.61°C.[7]).

Perchloric Acid Solutions: A known volume of 11.22 molar perchloric
acid was added to an equal volume of anhydrous acetic acid. The mix-
ture 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 I.

Table I

The Heat of Solution of Sodium Acetate in Water

Run	Grams NaOAc	Grams H_2O	ΔH(kcal./mole)
1	.4306 (A)	1070	-4.08
6	.5656 (A)	1072	-4.00
7	.7201 (B)	1064	-4.24

Inasmuch as the dilutions were so great, the extrapolation to infinite dilution shall be neglected; hence ΔH° = -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[7] and the value -4.08 kcal./mole (at 18°C.) given by Bichowsky and Rossini[8].

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[8] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, 1936.

Table II 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 .5997 g. NaOAc used in run 2; run 9 was carried out using the same acid plus .6443 g. NaOAc used in run 8. The average value, ΔH° = -4.8 kcal./mole, is taken for
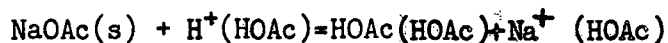
$$NaOAc(s) = Na^+(HOAc) + OAc^-(HOAc).$$

Table II

The Heat of Solution of Sodium Acetate in Acetic Acid

Run	Grams NaOAc	Grams HOAc	ΔH(kcal./mole)
2	.5997 (A)	1129	-4.70
3	.9264 (A)	1129	-4.70
8	.6443 (B)	1051	-4.91
9	.5963 (B)	1051	-4.93

Table III gives the details of four determinations of the heat of solutions of sodium acetate in acetic acid solution of perchloric acid. Run 5 was carried out using the same solution plus .8689 g. NaOAc used in run 4. The value ΔH° = -10.5 kcal./mole is taken for

$$NaOAc(s) + H^{+}(HOAc) = HOAc(HOAc) + Na^{+} (HOAc)$$

Hence ΔH° = 5.7 kcal./mole for

$$HOAc(HOAc) = H^{+}(HOAc) + OAc^{-}(HOAc),$$

the ionization of anhydrous acetic acid.

Table III

The Heat of Solution of Sodium Acetate in Acetic Acid

Solutions of Perchloric Acid

Run	Grams NaOAc	Grams $HClO_4$ Soln.	Molarity $HClO_4$	ΔH(kcal./mole)
4	.8689 (A)	1096	.376	-10.53
5	.7243 (A)	1096	.366	-10.52
10	.6523 (B)	1055	.248	-10.69
11	.5475 (B)	1117	.539	-10.38

Kolthoff and Willman[9] reported the ionization constant of anhydrous

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[9] I. M. Kolthoff and A. Willman, J. Am. Chem. Soc. 56, 1007-13 (1934).

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acetic acid to be 2.5×10^{-13} at 25°, and Kilpi and Puranen[10] reported

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[10] S. Kilpi and M. Puranen, Ann. Acad. Sci. Fennicae Ser. A, 57, No. 10, 3-12(1941); C. A. 38, 4855 (1944).

2.8×10^{-13}. Kolthoff and Willman note in their paper that emf measurements of Hall[11] and Hall and Conant[12] lead to a value of about 10^{-10}

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[11] N. F. Hall, J. Am. Chem. Soc. 52, 5115 (1930).

[12] N. F. Hall and J. B. Conant, J. Am. Chem. Soc. 49, 3047 (1927).

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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 vasis at 25°. Taking the density of acetic acid as 1.044 at 25°[13], this is corrected to $K = 2.4 \times 10^{-13} = (H^+)(OAc^-)$

[13] International Critical Tables, McGraw-Hill, New York, Vol. III, 1928.

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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

$$\Delta S^{\circ} = -38.6 \text{ cal./deg. mole.}$$

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.

The transfer of a gaseous ion to a solvent (ionic solvation) is attended to by two effects: the breakdown of the solvent structure, and the orientation of the polarized solvent molecules around·the ion in a dielectric medium. The first effect involves an increase in entropy; the second effect involves a decrease in entropy. In the following discussion, it is presumed that the first effect has been largely eliminated by considering only the solvation of "solvent ions", which should be more "at home" in the parent solvent than foreign ions. (Thus it is presumed that no disorder is created by introducing the NH_4^+ ion into liquid ammonia, for surely the NH_4^+ ion hydrogen-bonds with as many NH_3 molecules as does any other NH_3 molecule).

The ionization of a protonic solvent, HA, may be split up into three separate reactions:

I $2 HA (1) = 2 HA (g)$

II $2 HA (g) = H_2A^+(g) + A^-(g)$

III $H_2A^+(g) + A^-(g) = H_2A^+(HA) + A^-(HA)$.
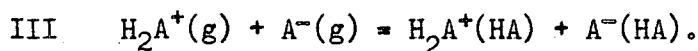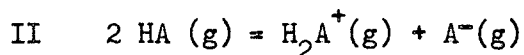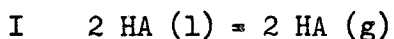
The entropies for the first step for acetic acid, ammonia and water, resp., are 62.2[14], 42.6[2,7] and 56.8[7] cal./deg. at 25°. The entropies

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[14]J. O. Halford, J. Chem. Phys. $\underline{9}$, 859 (1941).

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for the second step are small for these same molecules, being of the

order of magnitude of -4 cal./deg., and may be neglected. Therefore the differences between the entropies of ionization and the entropies of step I should approximate the entropies of step III, the solvation of the gaseous solvent ions. One calculates for step III, -101 cal./deg. for acetic acid, -92 cal./deg. for ammonia and -76 cal./deg. for water.

Powell and Latimer[15] have shown both empirically and theoreti-

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[15]R. E. Powell and W. M. Latimer, J. Chem. Phys. $\underline{19}$, 1139-41 (1951).

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cally that entropies of solvation are linearly related to the quantity $-\frac{nZ\mu}{Dr^2}$, where n is the number of solvent dipoles (with dipole moment μ) surrounding a point ion of charge Z at an average distance r, and where D represents the effective dilectric constant. It is significant that the values of $-\frac{nZ\mu}{Dr^2}$ for acetic acid, ammonia and water are qualitatively in the same order as the calculated entropies of solvation for the solvent ions of these solvents, if one assumes n to be the same for all three solvents.