the entire range of temperature within which the substances are liquid increase very slightly with temperature, indicating that the molecules contain no electric moments. The very small differences between the polarizations and the molar refractions extrapolated to infinite wave length for all of the substances show the absence of a measurable moment in their molecules. It is concluded that the atoms in a saturated hydrocarbon molecule may be joined together in every possible configuration without giving rise to any measurable lack of electric symmetry, although very small differences in the rigidity of binding of the electrons are detected. The electrical symmetry of the molecules gives no evidence of a difference in the electronegativities of the various constituent radicals.

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SOLUTIONS OF SALTS IN PURE ACETIC ACID. I. PRELIMINARY PAPER[1]

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Introduction

The study of the solubilities and chemical reactions of salts in non-aqueous solvents reveals certain analogies between these solutions and the more familiar solutions in water. These analogies have been most extensively developed, by the well-known researches of Franklin and his co-workers, for solutions in liquid ammonia. Despite the large amount of work that has been done with other non-aqueous solvents, our knowledge of such solutions is still so fragmentary that the accumulation and organization of much additional information would seem to be desirable.

In a previous paper,[2] the writer described an attempt to study the solubilities and reactions of salts in anhydrous sulfuric acid, a liquid of very different nature from those non-aqueous solvents which have been most widely examined. It was found that the range of investigation in this solvent was severely limited by the fact that, due to the large self-ionization of sulfuric acid, reactions of a solvolytic nature were of such general occurrence as greatly to interfere with the study of other reactions. It was decided to investigate, from the same point of view, solutions of salts in anhydrous acetic acid, this liquid being sufficiently polar in nature to be a fairly good solvent for many salts, while its self-ionization is apparently very small, since its specific conductivity is of the order of 2×10^{-8} reciprocal ohm.

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the St. Louis meeting, April, 1928.

[2] Davidson, THIS JOURNAL, **47**, 968 (1925).

The information that has hitherto been gathered concerning the solubilities and reactions of salts in acetic acid is decidedly meager. It was thought until rather recently that this liquid was a very poor solvent for inorganic salts.[3] Such data as have been obtained are very widely scattered. Many of the results of investigations previous to 1924 have been collected by Walden, in his "Elektrochemie Nichtwässriger Lösungen,"[4] although even here the data must be sought under several different headings. Quantitative measurements of solubility at various temperatures have been reported for mercuric chloride, uranyl nitrate, magnesium bromide and iodide, calcium chloride, antimony chloride and bromide, and the acetates of sodium and silver.[5] In addition, several addition compounds between salts and acetic acid have been isolated, including compounds with the acetates of the alkali metals,[6] and compounds with aluminum chloride, magnesium bromide and iodide, calcium chloride, antimony chloride and sodium iodide.[7] Conductivity measurements have been made on solutions of the alkali acetates and of several other salts.[8]

There have been a few scattered observations concerning reactions of metallic oxides with acetic acid, limited for the most part to the formation of acetates in which the metals exhibit unusually high valences.[9] The best known example of this is the formation of lead tetra-acetate from red lead.

Since the publication of Walden's text there have appeared, so far as the writer has been able to ascertain, three articles bearing on this subject. Webb[10] studied the activities of several salts in acetic acid solution, using the freezing-point method, and discussed the results on the basis of the assumption of practically complete ionization and the Debye-Hückel theory. Stranathan and Strong,[11] from the viscosities and conductivities of acetic acid–stannic chloride solutions, deduced the existence of an addition compound which, however, was not isolated. Still more recently, Hall and Conant,[12] in a study of hydrogen ion activities in what they

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[3] See, for instance, Beckmann, *Z. physik. Chem.*, **57**, 129 (1907).

[4] Bredig's "Handbuch der angewandten physikalischen Chemie," Vol. XIII, J. A. Barth, Leipzig, **1924**.

[5] (a) Étard, *Ann. chim. phys.* (7) **2**, 555 (1894); (b) Oechsner de Coninck, *Compt. rend.*, **132**, 90 (1901); (c) Menschutkin, *Z. anorg. Chem.*, **54**, 89 (1907); (d) Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **43**, 1785 (1911); *C. A.*, **6**, 1280 (1912); (e) Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921).

[6] For references on this subject see ref. 5 (e), p. 1479.

[7] (a) Walker and Spencer, *J. Chem. Soc.*, **85**, 1106 (1904); (b) Turner and Bissett, *ibid.*, **105**, 1777 (1914); also refs. 5 c, d.

[8] A summary of these measurements is given by Walden in "Das Leitvermögen der Lösungen," Leipzig, **1924**.

[9] See ref. 4, p. 378.

[10] Webb, THIS JOURNAL, **48**, 2263 (1926).

[11] Stranathan and Strong, *J. Phys. Chem.*, **31**, 1420 (1927).

[12] Hall and Conant, THIS JOURNAL, **49**, 3047, 3062 (1927).

propose to call "superacid" solutions, have described the neutralization of various organic bases by acids in glacial acetic acid, and have given some interesting speculations on the results, in terms of Brönsted's theory of acids and bases.

Object of the Present Work

In the investigation which is now in progress in this Laboratory, it is the writer's intention to extend the solubility data for salts in acetic acid by the determination of a large number of solubilities qualitatively, and a few typical ones quantitatively, and to make a study of reactions which take place between ionized salts in this medium, this being a field which has scarcely been touched. Only salts of inorganic bases will be considered.

The present paper reports the results of some preliminary experiments of a qualitative nature, which appear to the writer to be of interest. Quantitative experiments are in progress.

Experimental Part

The solvent used in these experiments was a special grade of c. p. glacial acetic acid, which had a melting point of 16.4°. The salts were of a reliable c. p. grade and were dried under suitable conditions. The anhydrous sulfuric acid used was prepared as described by Kendall and Carpenter,[13] and had a melting point of 10.4°.

1. **Solubilities of Salts in Acetic Acid.**—The number of salts which were found to be appreciably soluble was considerably larger than might be supposed from the meager data in the literature. The results of qualitative tests of solubility are given below.

The following salts were found to be readily soluble at room temperature: $LiNO_3$, $Ca(NO_3)_2$, NH_4NO_3, $Cu(NO_3)_2$, $CaCl_2$, $ZnCl_2$, $FeCl_3$, $SbCl_3$, BaI_2, ZnI_2, NH_4SCN, KCN, $LiC_2H_3O_2$, $KC_2H_3O_2$, $NH_4C_2H_3O_2$, $Pb(C_2H_3O_2)_2$, $Cd(C_2H_3O_2)_2$.

The following were found to be somewhat less soluble than the above: $AgNO_3$, $AlCl_3$, $HgCl_2$, HgI_2, $CoCl_2$.

The following were appreciably, though slightly, soluble (apparently less than one part in one hundred of solvent at ordinary temperature): NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, NH_4I, $NaNO_3$, KNO_3, $BaCl_2$, $KClO_3$, Na_2SO_4, $(NH_4)_2SO_4$, $Cu(C_2H_3O_2)_2$.

The following salts were found to be practically insoluble: AgCl, AgBr, AgI, AgCN, AgSCN, $PbCl_2$, PbI_2, HgCl, CdI_2, $Ba(NO_3)_2$, $Ca_3(PO_4)_2$, $Cu_3(PO_4)_2$, $CaCO_3$; also the sulfates of Li, K, Cu, Ag, Ca, Ba, Mg, Zn, Cd, Hg(-ous and -ic), Al, Pb, Mn, Ni, Co and Fe(-ous and -ic).

2. **Double Decomposition Reactions in Acetic Acid.**—Double decomposition reactions were found to take place in this solvent as readily

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[13] Kendall and Carpenter, This Journal, **36**, 2498 (1914).

as in water, the course of such reactions being determined largely by the solubilities of the several salts in question. In many cases these reactions were similar to familiar phenomena in aqueous solution. Thus silver chloride, bromide, iodide, cyanide and thiocyanate were each precipitated upon the addition of a solution of a salt containing the corresponding anion to a solution of silver nitrate. The silver cyanide precipitate, however, failed to dissolve in an excess of potassium cyanide solution. Lead chloride and lead iodide were precipitated from lead acetate solutions by sodium chloride and potassium iodide solutions, respectively. Solutions of cadmium acetate, lead acetate, zinc chloride, antimony chloride and silver nitrate all readily gave precipitates of the corresponding sulfides upon the introduction of hydrogen sulfide gas.

A solution of ferric chloride[14] gave, with ammonium thiocyanate solution, a deep red color, but no precipitate, just as in aqueous solution.

In many other cases, however, the reactions followed a less familiar course. A few examples of this will be described. When a solution of copper nitrate was treated with sodium acetate, a finely-divided, green crystalline precipitate of copper acetate was formed. A barium iodide solution, upon the addition of sodium nitrate, gave a finely-divided, white crystalline precipitate, which was shown to be barium nitrate. Any of the sulfates could be precipitated by the addition of a drop of anhydrous sulfuric acid, or a small amount of a solution of sulfuric acid in acetic acid, to a solution of a soluble salt of the metal in question. These came down as amorphous, flocculent precipitates from dilute solutions, or as gelatinous masses from concentrated ones. Even the sulfates of the alkali metals were readily precipitated in this way, although very dilute solutions of sodium and ammonium salts gave no precipitate. In connection with the general insolubility of sulfates in acetic acid, it is an interesting fact that sulfates which normally form hydrates can be precipitated in the anhydrous condition even when the solution contains some water. Thus, when *hydrated* cupric nitrate was dissolved in acetic acid and a little concentrated sulfuric acid added, a white precipitate of anhydrous cupric sulfate was obtained. Similarly, hydrated nickel nitrate gave yellow anhydrous nickel sulfate, and hydrated cobalt nitrate, pale pink anhydrous cobalt sulfate. It is worthy of notice that sulfates are insoluble in liquid ammonia, also.[15]

The only salt that was found to be noticeably solvolyzed by acetic acid was sodium carbonate with which, even at ordinary temperature, the solvent reacted fairly vigorously, with the evolution of CO_2. The reaction

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[14] According to Weinland, a solution of ferric chloride in 96% acetic acid contains the cation $Fe_3(C_2H_3O_2)_6^{+++}$. See, for instance, Weinland, Kessler and Bayerl, *Z. anorg. allgem. Chem.*, **132**, 209, 225 (1924).

[15] Franklin and Kraus, *Am. Chem. J.*, **21**, 8 (1899).

was, of course, not nearly so vigorous as in the case of aqueous acetic acid. Sodium bicarbonate was solvolyzed only very slowly, and calcium carbonate not at all.[16]

3. **Effect of Sodium and Ammonium Acetates upon Solubilities of Certain Other Salts.**—The acetates of the metals may be regarded as bases in acetic acid, since they presumably have the same negative ion as the solvent.[17] This being the case, it might be expected that in this solvent they would exhibit properties analogous to those of the hydroxides in water. The following observations support this hypothesis.

Zinc acetate is practically insoluble in acetic acid,[18] even at the boiling point. It was found, however, to dissolve quite readily in a sodium acetate solution (about 5 mole per cent. of sodium acetate). This is analogous to the solubility of zinc hydroxide in aqueous sodium hydroxide solution, and would appear to be due to the amphoteric nature of zinc. The solubility of copper acetate in acetic acid was not increased by the presence of sodium acetate.

Ammonium acetate, in acetic acid, may be regarded as the analog of ammonium hydroxide in water. That this analogy is far from being merely a formal one is indicated in a rather striking manner by the following facts. Zinc acetate was found to dissolve readily in ammonium acetate solution (about 5 mole per cent. of ammonium acetate), as does zinc hydroxide in water. Copper acetate, which was found to be only slightly soluble in acetic acid to give a greenish solution, and which could, in fact, be precipitated from a solution of a soluble copper salt by the addition of a small amount of ammonium acetate solution, not only dissolved readily in excess of this solution, but gave a dark blue color when so dissolved. When this solution was heated, its color gradually deepened, until at the boiling point it became a very intense purplish-blue, which was practically identical with the characteristic color attributed to the copper–ammonia ion in aqueous solution. On cooling this characteristic purplish tinge disappeared. It seems reasonable to suppose that ammonium acetate reversibly dissociates to some extent into free ammonia and acetic acid as the solution is heated, and that the purplish-blue color is due to an ion of similar nature to that which gives rise to it in aqueous solutions. Ammonium acetate was also found to dissolve other difficultly soluble salts, notably silver chloride, cupric sulfate, cobalt sulfate and nickel sulfate. All these phenomena are being investigated further, and will be discussed in a subsequent paper.

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[16] In connection with solvolysis by acetic acid, it should be mentioned that Rosenheim and Müller, *Z. anorg. Chem.*, **39**, 175 (1904), found that ferric chloride and ferric bromide crystallized from anhydrous acetic acid as $Fe(C_2H_3O_2)_2Cl$ and $Fe(C_2H_3O_2)_2Br$, respectively.

[17] Compare ref. 2, p. 969.

[18] See ref. 5e, p. 1478.

Summary

1. A fairly large number of salts, especially halides and nitrates, have been found to be soluble in acetic acid. All sulfates are very slightly soluble.
2. Double decomposition reactions have been found to take place quite readily in this solvent. A number of such reactions have been described.
3. Solvolysis does not occur in acetic acid solutions to any marked extent.
4. Analogies have been pointed out between the behavior of certain acetates in acetic acid and that of the corresponding hydroxides in water.

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THE MOLECULAR HEAT AND ENTROPY OF HYDROGEN CHLORIDE CALCULATED FROM BAND SPECTRA DATA

BY ELMER HUTCHISSON

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I. Introduction

It is well known that the heat capacity of gases decreases with temperature in the neighborhood of absolute zero. The temperature variation of the molecular heat of gaseous hydrogen chloride is especially interesting because it may be used to confirm the interpretation which the new quantum mechanics places upon band spectra. The computation of molecular heats, by means of the energy levels derived from band spectra, was first carried through by Hicks and Mitchell.[1] They made use of the spectral measurements of Imes and of Colby, Meyer and Bronk and assumed the "*a priori* probabilities" or weights of the quantum states to be 2, 4, 6, 8, etc., corresponding to those states characterized by the rotational quantum numbers $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, etc. Van Vleck[2] and others have pointed out that according to the new quantum mechanics the *a priori* probabilities must be 1, 3, 5, 7 for the states $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$ for simple polar molecules like HCl. Experimental proof that these probabilities are correct is furnished by Bourgin's[3] measurements of the absorption intensities of hydrogen chloride.

The band spectra measurements of Colby, Meyer and Bronk have been recalculated by Kemble,[4] who has obtained equations expressing the energy levels as a function of the vibrational and rotational quantum numbers.

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[1] Hicks and Mitchell, THIS JOURNAL, **48**, 1520 (1926).

[2] Van Vleck, *Phys. Rev.*, **28**, 986 (1926); see also Hutchisson, *ibid.*, **29**, 360A (1927).

[3] Bourgin, *ibid.*, **29**, 794 (1927).

[4] Kemble, *J. Opt. Soc. Am.*, **12**, 1 (1926).