[Contribution from the Chemical Laboratory of the University of Illinois]

THE EFFECT OF THE SOLVENT UPON THE ACTIVITY OF ACIDS: THE VAPOR PRESSURE OF HYDROGEN CHLORIDE IN GLACIAL ACETIC ACID SOLUTIONS

By Worth H. Rodebush and Roswell H. Ewart

The idea that the basicity of the solvent is an important factor in the ionization of acids has been discussed by many authors. Latimer and Rodebush[1] have given a discussion of the interaction of the attractive forces between solvent and hydrogen ion, by which the dissociation is largely determined.

More recently Conant, Hall and others have studied the behavior of acids in non-aqueous solvents by means of electromotive force measurements. Since the results of these measurements indicate a high degree of activity for the hydrogen ion, the term "superacid" has been employed to characterize the usual behavior of non-aqueous solutions of acid.

This term is something of a misnomer from the thermodynamic standpoint, since as has been pointed out by Taylor, Guggenheim[2] and others we do not measure individual ion activities, but rather the mean activity of a pair of ions. A further complication is the fact that the activity of the ions in the non-aqueous solvent is referred to the standard state of the water solution.[3]

Nevertheless the term has a certain justification since the behavior of the acid in solution probably depends chiefly on the coördination of solvent molecules by the hydrogen ion. The coördination number of the hydrogen ion is presumably two. In a basic solvent with high dielectric constant, the acid appears to be highly ionized. If the dielectric constant is low the

[1] For earlier references see (a) Abegg and Bodländer, Z. anorg. Chem., 20, 453 (1899); (b) Kraus and Bray, This Journal, 35, 1337 (1913); (c) Latimer and Rodebush, ibid., 42, 1419 (1920). The principal references to the recent literature are summarized in the following papers: (d) Conant and Hall, ibid., 49, 1412 (1927); (e) Hammett, ibid., 50, 2666 (1928); (f) La Mer and Downes, ibid., 53, 888 (1931); (g) Wynne Jones, J. Chem. Soc., 1065 (1930).

[2] Taylor, J. Phys. Chem., 31, 1478 (1927); Guggenheim, ibid., 33, 842 (1929).

[3] For a discussion of the difficulties involved here see Guggenheim, ibid., 34, 1540 (1930).

reaction between solvent and acid takes place just the same, but a hydrogen bond is now formed and the acid is not ionized.[1c]   In the same way an acid may react with an indicator without ionization.   The activity of an acid in solution therefore would seem to depend mainly upon the coördination of the solvent by the hydrogen ion and to a much less degree upon any physical property of the solvent as dielectric constant, especially as in most non-aqueous solvents the degree of ionization is small.

Hall and Werner[4] have pointed out that solutions of hydrogen chloride in acetic acid are not suitable for electromotive force measurements.   By the same token such solutions are suitable for vapor pressure measurements and the escaping tendency of the hydrogen chloride is measured directly. A PH measurement can only give the same thing with the attendant uncertainties of liquid junction potential.

It is not difficult to predict the behavior of an acid.   Suppose we have hydrogen chloride vapor at a partial pressure of 100 mm. in equilibrium with various solvents.   The escaping tendency of the hydrogen chloride must be the same in all solvents.   In water a very large amount of hydrogen chloride is dissolved, while in a solvent such as benzene, which cannot be coördinated by the hydrogen ion at all, the amount of hydrogen chloride is at most that predicted for an ideal solution.   The disparity between activity and concentration must therefore be very great provided the activities in both solutions are referred to a common standard state.   Or put in another way the escaping tendency of hydrogen chloride is very low from a 1.0 molal water solution and very high from a 1.0 molal benzene solution.   The same result must be obtained by any measurement of activity, for example, in reactions with indicators, regardless of whether water must be present to catalyze the reaction or not, since the activity is that of the vapor above the solution.

The behavior of an acid like perchloric is of course similar to that of hydrogen chloride.   It is not volatile and hence, provided it is miscible with a solvent, solutions of very high activity may be prepared.   On the other hand, since the normal state of a weak acid molecule in water is the unionized form and since this molecule may form a more nearly ideal solution with non-aqueous solvents than with water there is no reason why the activity of weak acids should appear to be increased in non-aqueous solvents.

In a solvent such as benzene which is not basic and which has a low dielectric constant, the ionization and the electrical conductivity must be very small indeed.   The change of conductivity with concentration in solutions of low dielectric constant was explained by Latimer and Rodebush;[1c] the explanation given by Gross and Halpern[5] comes to the same thing although expressed in a different terminology.

[4] Hall and Werner, This Journal, 50, 2367 (1928).
[5] Gross and Halpern, Physik. Z., 26, 636 (1925).

Experimental

General Method.—The vapor pressure of hydrogen chloride from glacial acetic acid solutions was determined by a dynamic method. A known volume of dry air was drawn through the saturating tubes which were filled with the solution. The air then passed through an absorption tube which removed the hydrogen chloride and acetic acid vapors. The quantities of hydrogen chloride and acetic acid vaporized were determined by analysis.

Description of Apparatus.—The general set-up of apparatus was similar to that of Pearce and Snow[6] except that the volume of air which passed through the saturators was determined by displacement of water, correction being made for temperature, total pressure and partial pressure of the water vapor of the measured volume of air. The saturators were of the type used by Bichowsky and Storch.[7] The absorption tube was of the same form as the saturator tubes. In order to prevent condensation on the walls of the connecting tubes, the absorption tube filled with standardized sodium hydroxide solution, as well as the saturators, was kept immersed in a thermostat held at 24.85 ± 0.02°.

Materials

Glacial Acetic Acid.—Three liters of Grasselli "Strictly c. p. Acid (99.5%)" was distilled from a five-liter flask over chromic oxide. The first and last 300 cc. were rejected. The middle portion was frozen slowly with almost constant agitation. The unfrozen center liquor was drained off. The frozen acid was then allowed to melt and was stored in sealed bottles. This now analyzed 99.7% acetic acid.

Saturation with Hydrochloric Acid.—Three hundred cc. of the pure acetic acid was partly saturated with dry hydrochloric acid gas. The hydrogen chloride was prepared by the action of c. p. 95% sulfuric acid on c. p. sodium chloride, and passed through a column containing glass wool to remove any sulfuric acid mist. This hydrogen chloride–acetic acid mixture was then diluted with the pure acetic acid as required. Previously, using the unpurified glacial acetic, the hydrogen chloride–acetic acid mixtures had a pale straw color. The mixtures using the purified acid were quite colorless.

Standard Solutions.—The standard acid was made up and its normality determined in the usual manner against standard sodium carbonate. The half normal sodium hydroxide which was used in the absorption tube was titrated against this acid. Chlorides were run gravimetrically and volumetrically by the Mohr and the Volhard methods. The Volhard method gave the best results and was used in all the final runs.

Manipulation.—The apparatus was sealed together and the saturators filled with about 140 cc. of the hydrochloric–acetic acid mixture. While this was being done a gentle stream of air was passed through the absorption tube to prevent acid vapors from collecting in this tube. The air stream was then turned off and 30.00 cc. of half normal sodium hydroxide was added from a buret to the absorption tube and then water was added until the top of the inner bubbler tube was just covered. These tubes were then sealed and the whole apparatus which was held in a frame was lowered into the thermostat and sealed to the displacement bottle. It was necessary to have a small constriction in the line from this bottle to the absorption tube in order to prevent irregularities in flow which would otherwise cause the air to by-pass through the holes in the bottom of the bubbler tubes and thus it might not become completely saturated.

The measurement of the displaced air was started when the first bubble appeared

[6] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

[7] Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

in the absorption tube.   When one liter of the water, which had been previously satu-
rated with air, had been displaced the flow was shut off.   The manometer on the dis-
placement bottle was read as soon as equilibrium was reached.   The temperature of
the water in this bottle was taken and the contents of the absorption tube analyzed.
The hydrochloric–acetic acid mixtures were analyzed before and after each run.   The
variation was usually less than 3% and by using the average analysis very little error
is introduced.

The vapor pressures were calculated using the equation

$$P = \frac{(P_1 - P_3)}{(P_2 V_2/mRT_2 + 1)}$$

TABLE I

ANALYTICAL DATA AND CALCULATED VAPOR PRESSURES OF HYDROCHLORIC ACID

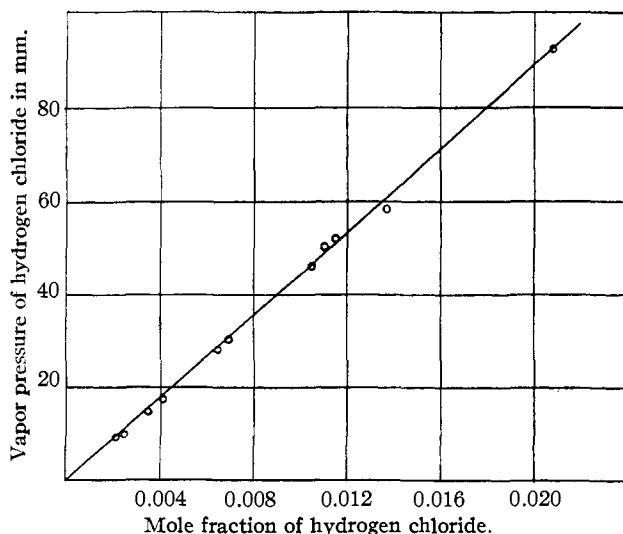| Run	P_1, pressure in mm.	V_2, liters (vol. of air = vol. of water)	Partial press. of air	T_2, air temp. °K.	m, HCl, mole of HCl in absorption tube	m, AcOH mole of AcOH in absorption tube	C, av. % HCl in glacial AcOH	N_2 mole fraction of HCl in glacial AcOH	P, partial vapor press. of HCl, mm.
24	746.0	1.000	722.2	296.8	0.005700	0.001619	1.270	0.0208	93.0
25	745.6	1.000	720.9	297.4	.003406	.001559	0.836	.0137	58.8
15	739.6	1.000	718.4	294.5	.003079	.001589	.70	.0115	52.8
16	742.9	1.000	718.8	297.2	.002920	.001698	.67	.0110	50.9
17	749.6	1.000	724.9	297.2	.002669	.001667	.640	.0105	46.9
18	744.8	1.051	721.2	297.4	.001852	.001680	.423	.00695	31.6
19	743.7	1.000	715.8	298.6	.001570	.001643	.385	.00632	28.6
20	747.5	1.000	723.9	296.7	.000946	.001616	.247	.00406	17.3
21	746.7	1.000	717.5	299.8	.000806	.001588	.212	.00349	15.0
22	741.7	1.013	715.9	297.6	.000514	.001725	.125	.00206	9.4
23	744.1	1.000	718.3	297.5	.000524	.001690	.147	.00242	9.7

Fig. 1.—Vapor pressure of hydrogen chloride from glacial acetic
acid solutions at 24.8°.

where P_3 is the vapor pressure of acetic acid or 15.6 mm.[8] at 25°, and m is the number of moles of hydrochloric acid in the absorption tube. The other symbols are as given in Table I.

Results.—The vapor pressure curve over the range studied is a straight line function of the mole fraction. It may be seen that since the partial vapor pressure of the hydrogen chloride from a glacial acetic acid solution for which the mole fraction of hydrogen chloride is 0.011 is 50.9 mm. and since the corresponding partial vapor pressure from an aqueous solution of the same mole fraction is only about 0.0001 mm.,[9] the relative activity is more than a hundred thousand times greater in the former case. Earlier results on much stronger solutions indicate a sharp increase in the slope of the curve. The following approximate results are given: 5% hydrochloric acid, 470 mm.; 3% hydrochloric acid, 300 mm.

Summary

A discussion is given of the effect of solvent upon the activity of acids in solution together with measurements of the vapor pressure of hydrogen chloride in glacial acetic solution.

[8] "International Critical Tables."

[9] *Ibid.*, Vol. 3.

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# THE THERMODYNAMIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 0 TO 40°

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Although flowing amalgam cell measurements have been used with considerable success to determine the activity coefficients of alkali and alkaline earth halides at 25°, few reliable measurements are available at other temperatures. The present communication contains electromotive force measurements of the cells

$$\text{Ag} \mid \text{AgCl} \mid \text{NaCl} \ (m_2) \mid \text{Na}_x\text{Hg} \mid \text{NaCl} \ (0.1) \mid \text{AgCl} \mid \text{Ag}$$
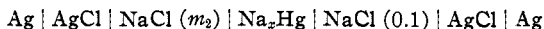
from which the activity coefficient and partial molal heat content of sodium chloride have been computed through a concentration range from 0 to 4 M and a temperature range of from 0 to 40° at 5° intervals.

Experimental Procedure and Results

All precautions pertaining to accurate flowing amalgam cell measurements were taken.[2] A vacuum technique was employed which excluded

[1] This paper contains the material and calculations originally presented by Leslie F. Nims to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Harned, THIS JOURNAL, **51**, 416 (1929).