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The Partial Pressures of Formic and Acetic Acids above Some Aqueous Solutions; and Their Partial Molal Free Energies at 1.0 Molal Concentration

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The paucity of data pertaining to the vapor pressures of aqueous solutions of the organic acids has hitherto retarded thermodynamic calculations in this field. In the present study the partial pressures of formic acid above three of its solutions and those of acetic acid above two solutions have been measured at 25°C. From these results the partial molal free energies at 1.0 molal concentration have then been derived.

EXPERIMENTAL METHOD

THE method employed was essentially similar to that which Bates and Kirschman¹ used in their investigation of the vapor pressures of the hydrogen halides in aqueous solution. It here involved the determination of the formic or acetic acid contained in a given quantity of nitrogen in equilibrium with the particular aqueous solution and a comparison of this with the amount of water vapor which the same sample of nitrogen contained when in equilibrium with pure water at the same temperature. From a knowledge of the vapor pressure of water (0.00313 atm. at 25°²) and the constants for the vapor-phase equilibria between the double and single molecules of the organic acid, the vapor pressures of the acids could then be computed.

The apparatus consisted of a train of saturators and absorbers through which nitrogen was passed; it was immersed in a thermostat at 25°C ($\pm 0.02^\circ$). In the successive parts of the apparatus the nitrogen sample was (I) saturated with vapor from the aqueous solution that was being studied, next (II) passed through absorbers in which the acid vapor was absorbed by standard NaOH solution and later determined by titration, then (III) passed through saturators in which saturation with the vapor of pure water was completed, and finally (IV) passed through an absorber containing "Dehydrite" in order to determine this weight of water vapor. The usual

precautions and tests¹ were made to insure the completeness of the saturation and absorption in the various parts of the gas train, and a correction was introduced for the change in volume of the nitrogen sample accompanying the small drop of pressure (9 mm of mercury) between the final saturator for the acid solution in I and the "Dehydrite" absorber in IV. Four to six acceptable determinations were made upon each of the solutions studied; the results of these determinations seldom differed from the mean values reported in Table I (column 2) by more than 2 percent, except in the case of the most dilute formic acid solution. Here, due largely to the low vapor pressure, the average deviation of the four values was 8 percent.

VAPOR PRESSURE DATA

The vapor pressure data are summarized in Table I. Column 1 contains the concentrations of the several solutions, expressed in mols of acid per 1000 g of water. The pressure values in

TABLE I. *Vapor pressure data at 25°C.*

	Molality	P_f (atm.)	P_d (atm.)	P_s (atm.)
Formic acid	0.510	0.000115	0.000004	0.000108
	1.164	0.000245	0.000016	0.000214
	2.285	0.000476	0.000049	0.000378
Acetic acid	1.316	0.000345	0.000055	0.000235
	2.890	0.000830	0.000194	0.000441

column 2 are those computed directly from the quantities of acid and water found in the absorbers on the assumption that the molecular

¹ Bates and Kirschman, *J. Am. Chem. Soc.* **41**, 1991 (1919).

² International Critical Tables, Vol. III, p. 212.

weights of the acids are the same as their formula weights. Inasmuch as some of the acid molecules in the vapor state are polymerized or "double" molecules, this assumption is not true and accordingly these values are designated as fictional pressures (P_f). If P_s is the pressure of the simple or "single" acid molecules in the vapor, that of the double molecules becomes $P_d = \frac{1}{2}(P_f - P_s)$; and a condition of equilibrium between the two types of molecules must exist to satisfy the relationship $P_s^2/P_d = K_p$. Taking 0.0029 for the value of K_p for formic acid vapor from the work of Ramsperger and Porter³ and 0.001 for K_p for acetic acid from the calculations of Parks and Huffman,⁴ we have thus been able to deduce the values of P_d and P_s given in columns 3 and 4.

In the case of acetic acid our results for P_f differ by about 6 percent from those obtained recently by Fredenhagen and Liebster,⁵ although our figures for P_s differ by a considerably larger amount because we have here employed a different value for K_p .

SOME DERIVED FREE ENERGY DATA

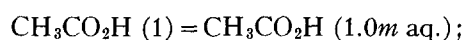
With the aid of the preceding vapor pressure data and Henry's law we have estimated $P_s = 0.000191$ atm. for 1.0 molal formic acid solution and $P_s = 0.000184$ atm. for 1.0 molal

acetic acid solution. Taking $P_s = 0.0117$ atm. in the vapor above pure formic acid³ at 25°C, we then find for the free energy change in the transfer of one formula weight of formic acid from the pure state into a 1.0 molal aqueous solution



$$\Delta F_{298} = RT \ln 0.000184/0.0117 = -2440 \text{ cal.}$$

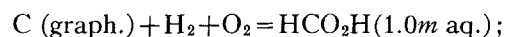
Similarly, taking $P_s = 0.004$ atm. in the vapor above pure acetic acid⁴ at 25°, we have for the free energy of dilution of this acid



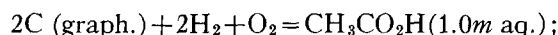
$$\Delta F_{298} = -1820 \text{ cal.}$$

Our result for the free energy of dilution of formic acid differs by 520 calories from that ($\Delta F_{298} = -2960$) calculated by Ramsperger and Porter from Branch's data.⁶ However, it should be noted that Branch worked with an aqueous solution of formic acid which was also 0.5 molal with respect to HCl and hence the dilution conditions are not quite comparable.

Combining these free energy changes with the values given by Parks and Huffman⁷ for the free energies of formation of the pure liquid acids, we then obtain the partial molal free energies of the two acids in a 1.0 molal aqueous solution



$$\Delta F_{298}^\circ = -87,590 \text{ cal.};$$



$$\Delta F_{298}^\circ = -96,320 \text{ cal.}$$

³ Ramsperger and Porter, J. Am. Chem. Soc. **48**, 1267 (1926).

⁴ Parks and Huffman, *The Free Energies of Some Organic Compounds*, p. 143, The Chemical Catalog Co., New York, 1932.

⁵ Fredenhagen and Liebster, Zeits. f. physik. Chemie **A162**, 449 (1932).

⁶ Branch, J. Am. Chem. Soc. **37**, 2316 (1915).

⁷ Parks and Huffman, reference 4, p. 231.