[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

# Solubilities of Some Strong Electrolytes in the Hydrogen Peroxide–Water System.[1] I. Sodium Chloride, Fluoride and Nitrate, Potassium Chloride and Nitrate, and Lithium Nitrate

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The solubilities of sodium chloride, potassium chloride, lithium nitrate, sodium nitrate, potassium nitrate and sodium fluoride have been determined in the full range of concentrations of hydrogen peroxide–water solutions at 25, 15 and 0°. The solubility of sodium chloride is almost independent of temperature over the concentration range. Sodium nitrate, potassium nitrate and lithium nitrate have an approximately constant temperature dependence over the whole concentration range. Potassium chloride showed little temperature dependence in concentrated hydrogen peroxide solutions and appreciable dependence in water-rich solutions. The solubility of sodium fluoride in hydrogen peroxide was much more dependent on temperature than in water and increased as the temperature was lowered from 25, to 15, to 0°. The solubilities of sodium chloride, sodium nitrate and lithium nitrate are greater in water than in hydrogen peroxide whereas those of sodium fluoride, potassium chloride and potassium nitrate are greater in hydrogen peroxide. Lithium and potassium nitrates show definite discontinuities in the curves for mole fraction hydrogen peroxide in solvent *versus* molality of salt.

## I. Introduction

In spite of numerous attempts at generalization, the problem of explaining even semi-quantitatively the solubility relationships of salts in water and similar hydrogen bonding solvents remains a baffling one. In view of the close similarity of hydrogen peroxide and water, it was thought that a study of the solubility of typical salts in mixtures of these two solvents might throw light on the general problem.

The present paper gives the results of determinations of the solubilities in hydrogen peroxide–water mixtures for a number of the alkali metal salts of some of the simpler anions. Solubility determinations have been made over the full range of concentrations of hydrogen peroxide–water mixtures for NaCl, KCl, $LiNO_3$, $KNO_3$, $NaNO_3$ and NaF at 25, 15 and 0°.

## II. Experimental

The hydrogen peroxide[3] used as a starting material for most of these measurements was 90% by weight, or in the most concentrated tests, 98%. For solubilities at the highest concentrations of hydrogen peroxide and for those samples that showed any evidence of decomposition, further purification of the hydrogen peroxide was carried out by distillation following Gross and Taylor.[4] All salts used were of reagent grade. For any of the salt solutions showing any appreciable evidence of decomposition a further purification of the salts was carried out by recrystallization. The solubilities were determined by adding hydrogen peroxide of the desired concentration to an excess of salt contained in a 25-ml. volumetric flask. The solutions were placed immediately in the 0, 15 or 25° thermostat and rocked at about 5 oscillations per minute until equilibrium was attained. In most cases this was attained within 24 hours. The temperature was controlled to better than 0.02°.

Samples of a particular solution were removed for analysis at several intervals in order to ensure attainment of equilibrium. Analyses of each sample were carried out in triplicate for hydrogen peroxide concentration and in duplicate for salt concentration. The hydrogen peroxide concentration was determined by titration with potassium permanganate using the method of Huckaba and Keyes.[5] The salt concentrations were determined by dry weight analysis.

## III. Results

The results for the individual salts at the three temperatures are shown in Figs. 1 through 6 and are summarized for comparison at 25° in Fig. 7 as the differences between the molal solubility in the mixtures of hydrogen peroxide and water and that in water plotted against the mole fraction of hydrogen peroxide in the solvent mixture. The molal deviation of the less soluble $LiNO_3$ is not shown in Fig. 7 due to insufficient data. It can be seen that the present results check well with earlier more limited solubility determinations in this system of Åkerlöf and Turck.[6] Also the solubility determinations in pure hydrogen peroxide at 25° by Maass and Hatcher,[7] Matheson and Maass,[8] and Kaza-

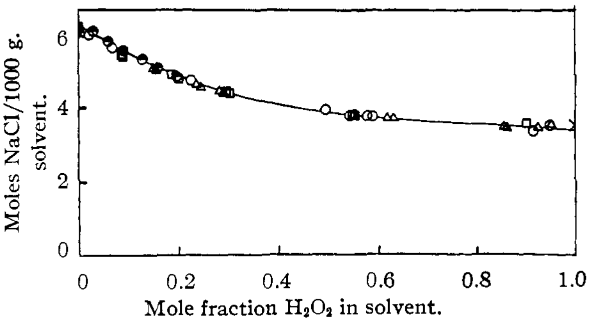

Fig. 1.—Solubility of NaCl in $H_2O_2$–$H_2O$ solutions at 0, 15 and 25°: ○, 25°; □, 15°; △, 0°; ◓, Åkerlöf and Turck; ×, Maass and Hatcher; ●, Berkeley.

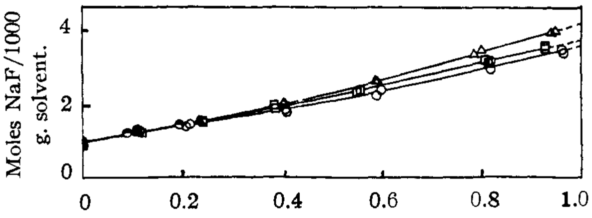

Fig. 2.—Solubility of NaF in $H_2O_2$–$H_2O$ solutions at 0, 15 and 25°: ○, 25°; □, 15°; △, 0°; and ◓, Åkerlöf and Turck; ●, Payne.

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[2] This paper is based in part on a portion of the thesis submitted by J. D. Floyd in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of the University of Virginia, June 1953.

[3] The 90 and 98% hydrogen peroxide used as starting material was donated by the Buffalo Electrochemical Company.

[4] P. M. Gross, Jr., and R. C. Taylor, THIS JOURNAL, **72**, 2075 (1950).

[5] C. E. Huckaba and F. G. Keyes. *ibid.*, **70**. 2578 (1948).

[6] G. A. Åkerlöf and H. E. Turck, *ibid.*, **57**, 1746 (1935).

[7] O. Maass and W. H. Hatcher, *ibid.*, **44**, 2472 (1922).

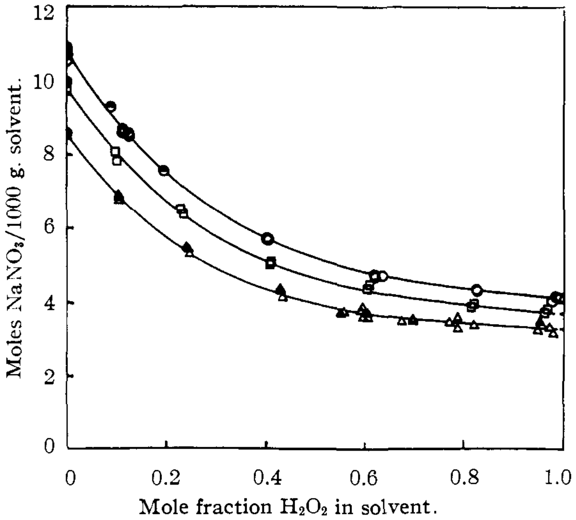

Fig. 3.—Solubility of NaNO$_3$ in H$_2$O$_2$–H$_2$O solutions at 0, 15 and 25°: O, 25°; □, 15°; Δ, 0°; ◐, Åkerlöf and Turck; ●, Berkeley.

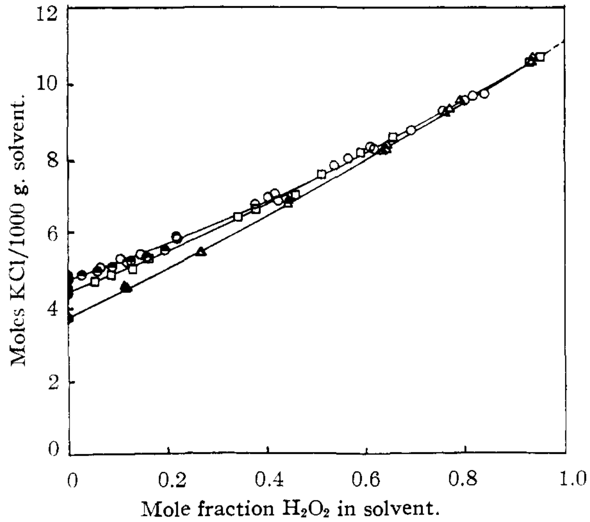

Fig. 4.—Solubility of KCl in H$_2$O$_2$–H$_2$O solutions at 0, 15 and 25°: O, 25°; □, 15°; Δ, 0°; ◐, Åkerlöf and Turck; ●, Tilden and Shenstone.

netzkii[9] are consistent with these results. Our solubilities in water were also consistent with earlier work.[10–12] Inspection of the figures will reveal several points of general interest.

With the possible exception of the case of KCl, salts made up of the simple monatomic anions and cations investigated show but little temperature dependence of solubility as solvent medium changes. This is particularly striking in the case of NaCl and might indicate either strong solvation of the anion or cation or both or an unusual compensation effect as the temperature changes. By contrast the salts with the more complicated NO$_3^-$ anion show: (1) greater temperature dependence; (2) less disparity in temperature dependence over the changing solvent range, and (3) in general a much greater effect of solvent composition on solu-

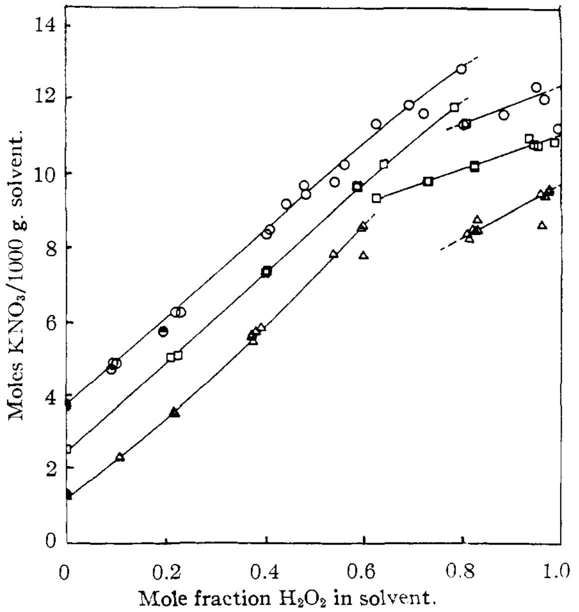

Fig. 5.—Solubility of KNO$_3$ in H$_2$O$_2$–H$_2$O solutions at 0, 15 and 25°: O, 25°; □, 15°; Δ, 0°; ◐, Åkerlöf and Turck; ●, Berkeley.

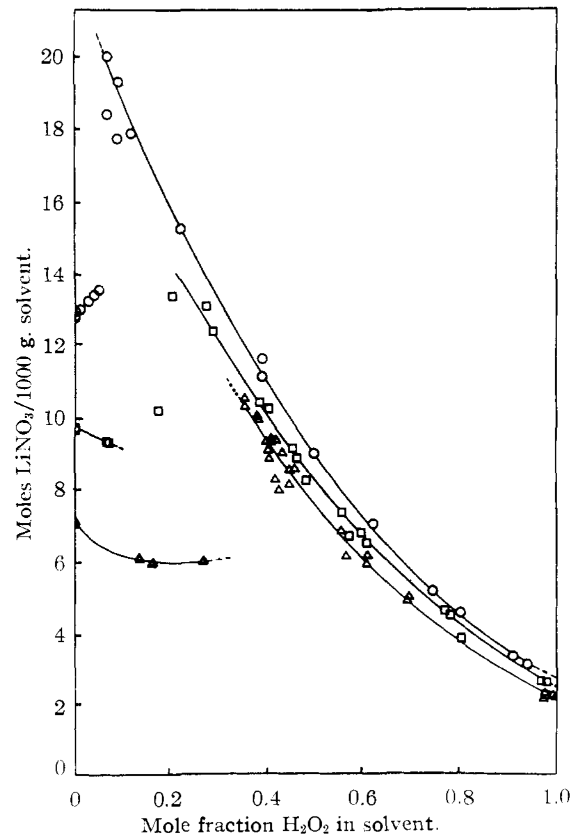

Fig. 6.—Solubility of LiNO$_3$ in H$_2$O$_2$–H$_2$O solutions at 0, 15 and 25°: O, 25°; □, 15°; Δ, 0°.

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[8] G. L. Matheson and O. Maass, THIS JOURNAL, **51**, 675 (1929).

[9] P. V. Kazanetzkii, *J. Russ. Phys. Chem. Soc.*, **46**, 1110 (1914); *C. A.*, **9**, 2843 (1915).

[10] Earl of Berkeley, *Phil. Trans. Roy. Soc. (London)*, **203A**, 189 (1904).

[11] J. H. Payne, THIS JOURNAL, **59**, 947 (1937).

[12] W. A. Tilden and W. A. Shenstone, *Proc. Roy. Soc. (London)*, **35**, 345 (1883).

bility. It seems obvious that highly specific ion effects are involved.

In attempting to account qualitatively for these effects it is useful in first approximation to regard the water molecule as a sphere of relatively small size with a pair of centers (the hydrogen bonding functions) of positive charge located at two corners of a slightly distorted regular tetrahedron and with two centers of negative charge at the remaining corners.[13] The preponderance of physical evidence points to a skew structure for hydrogen peroxide in which the two oxygen atoms are joined by a covalent bond and the OH bonds make angles of approximately 100° with the line of oxygen centers and about 82° with each other.[14,15] Again in first approximation this model results in a molecule with two centers of positive charge (the hydrogen bonding functions) at two corners of a still further distorted regular tetrahedron and two centers of negative charge at the remaining corners. Because of the separation of the oxygen centers by about 1.5 Å. there is substantially greater separation of the centers of positive charge and the centers of negative charge in the case of the hydrogen peroxide compared to water. Thus in terms of this crude approximation $H_2O$–$H_2O_2$ mixtures may be regarded as having the same number and kind of centers of charge per molecule but with increasingly large separation of like charges as the mole fraction of hydrogen peroxide is raised. It seems evident that ion size considerations will be of first importance in determining ion solvation as these molecules change with solvent composition.

It is of interest to attempt to interpret the present results in the light of this crude picture. An inspection of the figures shows clearly that the cation size is playing a dominant role in determining solubility in the chloride and nitrate series. The smaller size of the lithium and sodium ions favors solubility in the water-rich mixtures, whereas the reverse is true for the salts of the larger potassium ion. This generalization regarding dominance by the cation fails to hold in the case of sodium fluoride with its small cation, but even in this case bears out the general thesis that ion size is of first importance in determining solubility relations in this system. Additional confirmation of this general interpretation is afforded by the appearance of the new solid solvate phases separating in the case of $LiNO_3$ (Fig. 6) from the water-rich solvents and in the case of $KNO_3$ (Fig. 5) from the peroxide-rich mixtures.

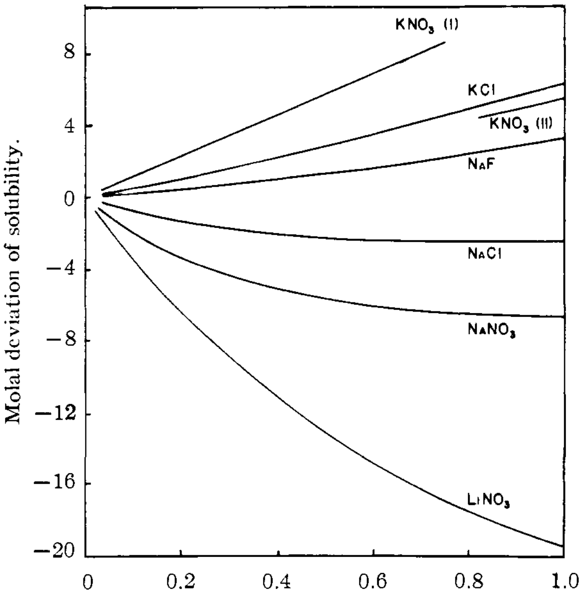

Fig. 7.—Molal deviation of solubility in $H_2O_2$–$H_2O$ solutions from solubility in $H_2O$ at 25°.

The results of Gorin[16] provide further general confirmation for the interpretation outlined here. He found from distribution measurements of hydrogen peroxide between isoamyl alcohol and aqueous salt solutions that there was a strikingly large decrease in the activity of the hydrogen peroxide in the case of potassium chloride. This he interpreted as a strongly preferential solvation of the potassium ion by the hydrogen peroxide molecules in comparison with similar sodium salts.

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[13] Compare for example: H. Frolich, "Theory of Dielectrics," Clarendon Press, Oxford, 1950, p. 140.

[14] W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publ. Corp., New York, N. Y., in press.

[15] Also G. B. B. Sutherland and W. G. Penney, *Trans. Faraday Soc.*, **30**, 898 (1934).

[16] M. H. Gorin, THIS JOURNAL, **57**, 1975 (1935).