Humidity Fixed Points of Binary Saturated Aqueous Solutions

Lewis Greenspan

Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234

(October 22, 1976)

An evaluated compilation of equilibrium relative humidities in air versus temperature from pure phase to approximately 10⁵ pascal (1 atm) in pressure is presented for 28 binary saturated aqueous solutions. The relative humidities of the solutions range from about 3 to 98 percent. Using a data base from 21 separate investigations comprising 1106 individual measurements, fits were made by the method of least squares to regular polynomial equations with two through four coefficients. Equations and tables are presented along with the estimated uncertainties in the correlated results.

Key words: aqueous solution; equilibrium; humidity; relative humidity; salt; saturated salt solution; vapor pressure; water vapor.

Introduction

Research, hygrometer calibration, testing and material conditioning often require the accurate control of humidity in a working space. The common methods of controlling the humidity accurately use either a humidity generator [1A]¹ or the equilibration of a closed space with a chemical system [1B] which produces the desired equilibrium vapor pressure.

Humidity generators tend to be expensive and complex whereas equilibration with chemical systems that provide fixed points is a relatively inexpensive and simple method of humidity control. Among the chemical systems used for this purpose are aqueous sulphuric acid solutions, glycerine and water solutions and single and binary salt solutions. Each such solution offers a degree of humidity adjustment that can be achieved by changing its concentration. On the other hand, special problems are associated with the use of solutions because their concentrations must be measured and controlled. Not only must the concentration of the solution be determined initially but the presence of any humidity sources or sinks in the controlled space and even the initial equilibra-

tion process of the space can alter the solution concentration.

An especially useful method of humidity control by chemical system involves the use of binary saturated aqueous solutions (primarily of single salts) in which the solute is highly non-volatile.

At any temperature, the concentration of a saturated solution is fixed and does not have to be determined. By providing excess solute, the solution will remain saturated even in the presence of modest sources or sinks. Where the solute is a solid in the pure phase, it is easy to determine that there is indeed saturation. Due to the ease of its use, this is a popular method of humidity control.

Since a given saturated salt solution provides only one relative humidity (RH) at any desired temperature, a different relative humidity must be achieved by selecting another appropriate salt. Though much data on saturated salt solutions have been produced and many compilations of the equilibrium relative humidities of selected saturated salt solutions exist, there are no compilations for which the data have been critically analyzed and estimates of the uncertainties involved given, a step which is abolutely essential to the

implimentation of the concept of fixed points.

We have moved to fill this gap by compiling, from the literature, data on a sufficient variety of saturated salt solutions to cover the entire range of relative humidity at reasonably close intervals. We have adjusted these data [1-21] to be consistent with temperatures on IPTS-68 and the most recent equations for the vapor pressure of water [22]. We have also analyzed the experimental techniques used in obtaining the original data and have made estimates of the uncertainties in the original data. We have then used these data to calculate "best" values of relative humidity in air as a function of temperature from pure phase to approximately 105 pascal (1 atm) in pressure for these saturated solutions.

Background

The methods used by investigators to determine the water vapor in equilibrium with saturated salt solutions are diverse. A short description of the various methods used in the

referenced papers is of interest.

(1) The direct measurement of the vapor pressure. A chamber containing a saturated salt solution at a controlled temperature is first evacuated to remove all gases. Evaporation from the solution is then allowed to proceed until the ambient vapor, essentially all water, has come to equilibrium with the solution and a direct determination of the total pressure within the chamber is made by conventional pressure measurement techniques.

(2) Dew point measurement. The dew point of the gas within a chamber containing a saturated salt solution at controlled temperature is measured by means of a cooled mirror within the chamber. Using vapor pressure tables or equations, this dew point is converted to the vapor pressure of water.

(3) Isopiestic vapor pressure measurement. The vapor pres-

¹ Figures in brackets indicate the literature references at the end of this paper.