

sure of a saturated salt solution in one cell or chamber is allowed to come to equilibrium with a cell or chamber containing a reference solution at a fixed temperature. The reference solution must be well characterized as to vapor pressure as a function of concentration at the reference temperature. Under the equilibrium condition, the equilibrium vapor pressure of the saturated salt solution is identical to the equilibrium vapor pressure of the reference solution. After the two cells have reached equilibrium, the concentration of the reference solution is determined (usually by weighing) and the vapor pressure is calculated.

(4) *Relative vapor pressure measurement.* A chamber containing a saturated salt solution and a chamber containing pure water or other well characterized solution are each evacuated to remove all non-water vapor gases. The two chambers are maintained at the same temperature and the absolute pressure of the saturated salt solution is measured as in the first method. In addition the pressure difference between the two chambers and/or the pressure of the reference solution is determined. The ratio of the vapor pressure of the saturated salt solution to the vapor pressure of the water is the activity (or relative humidity) of the saturated salt solution.

(5) *Measurement with a calibrated humidity sensor.* A chamber containing a saturated salt solution and a humidity sensor are brought to equilibrium at a controlled temperature. Calibration of the sensor before or/and after the measurement provides the means of determining the equilibrium vapor pressure.

(6) *Gravimetric determination.* Dry gas is passed through the binary saturated solution at a fixed temperature. The water vapor in the effluent gas is absorbed by a desiccant and measured by weighing. The volume of the gas is also determined. From these the vapor pressure or the mixing ratio can be determined.

As one would imagine, the errors associated with these methods differ as to source and magnitude. The errors in any of the methods are also functions of the level of vapor pressure being measured as well as the temperature of the saturated salt solution. There is, therefore, probably no one method that gives a best measurement under all conditions.

### 3. Method

We have accumulated experimental data from various researchers [1-21] and calculated "best" values of relative humidity and the associated uncertainties of those values. Typical methods of calculating or recalculating the relative humidity and associated uncertainties for the various investigations are given in the Appendix. Our data base consists of 21 investigations and includes some of the most cited work in the field. In total, 1106 individual calculations of relative humidities and associated uncertainties were made which involved 89 saturated solutions. Not all data nor all saturated solutions in this study were found satisfactory for use.

The original data were corrected to be consistent with temperature on IPTS-68, with the most recent formulation for the vapor pressure of water [22] and with the most recent equations for the enhancement of water vapor in air [23]. The computed relative humidity data were then collated and fitted by the method of least squares to regular polynomials as a function of temperature in degrees Celsius (IPTS-68). In the fitting process, each datum was weighted inversely proportional to the estimated uncertainty of the datum. The order of the polynomial used in the fit was determined by an F-test or

by analysis of the result of fits to various orders. An arbitrary decision was made not to use any order higher than 3. Also, no data at temperatures below 0 °C or above 104 °C were used in the fits.

In the fitting process, the standard deviation of the predicted value was computed for each datum. These standard deviations were themselves fitted to a quadratic equation, as a function of temperature, by the method of least squares. At any desired temperature for a given saturated salt solution, the standard deviation of the predicted value was calculated using the appropriate quadratic equation. Three times this value was then assigned as the estimated uncertainty for the corresponding value of relative humidity, with certain exceptions discussed below. This is the value which appears in table 2.

Where a number of investigations of the same solution existed and the relative humidity vs temperature results of one investigation were completely inconsistent with the results of the other investigations, the data of the deviant investigation were eliminated and a new fit made.

The data used in this paper met one of the following criteria: (1) a large number of investigations were included and exhibited a small residual standard deviation of the relative humidity vs temperature fits; (2) although few investigations were included, the method of measurement was judged to be superior and estimates of the uncertainties of the original measurements themselves were small; and (3) the data were in a relative humidity range which was not approximated by any of the other binary saturated solutions.

### 4. Results

Table 1 contains coefficients for the data of the selected salts fitted to an equation of the form:

$$RH = \sum_{t=0}^3 A_t t^t$$

where  $RH$  is in percent and  $t$  is in °C (IPTS-68). The salts are listed in ascending order of  $RH$  at 25 °C. Also included in table 1 is the residual standard deviation of the fit, the range of temperature over which the fit was performed and references for the fundamental data that were involved in that particular fit.

Table 2 gives the calculated relative humidities for each of the binary saturated solutions at 5-degree intervals along with the estimated uncertainties in relative humidity at each of the temperatures. The saturated salt solutions are presented in the same order as in table 1.

### 5. Discussion

Although the method used for fitting the data gave no problems, the assignment of weights to each datum required some judgment. Three methods of weighting were considered: (1) weights were assigned inversely proportional to the variance of the individual datum where the variance was taken as the square of the total uncertainty; (2) weights were assigned inversely proportional to the estimated total uncertainty of the individual datum; and (3) weights of unity were assigned to all data.

All of the data were fitted three times, once for each type of weighting. The results were assembled into three tables of