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THERMODYNAMIC PROPERTIES OF MOIST AIR CONTAINING
1000 TO 5000 PPM$_V$ OF WATER VAPOR

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Abstract: This paper provides calculated values of water vapor density, enthalpy, entropy, and Gibbs free energy associated with moist air. They cover the range of interest in moisture control and measurement methods for microelectronic packages from water vapor concentration of 1000 to 5000 PPM$_V$. These values are essential for establishing moisture standards for IC package gas analysis, for developing new measurement techniques for accurate determination of a known water vapor content, and for improving the understanding of moisture absorption/desorption phenomena in small or large chip packages. All values are referred to the recent realization of the International Temperature Scale of 1990 (ITS-90).

Molar enthalpy, molar entropy, and molar Gibbs free energy of moist air are expressed explicitly in terms of the associated water vapor density. The values of the molar quantities are the sum of three parts due to: (1) the mole fraction of water vapor, (2) the mole fraction of dry air, and (3) the effects of interaction between air molecules and water molecules.

Key Words: Microelectronic package; mixture; moisture standards; molecular interaction; thermodynamics; water vapor.

1. INTRODUCTION

Moisture measurement and control for microelectronics requires accurate and reproducible determination of water vapor concentration in moist air. The current Method 1018 has been implemented by both commercial and semiconductor manufacturers' analytical facilities as part of MIL-STD-883 for measuring water vapor content within a microelectronic package. In several correlation experiments, the participating laboratories performed mass spectrometric measurements of various moisture levels [1]. Devices were designed and packaged with three different cavity volumes and two different sealing technologies to contain moisture in the range of 2000 to 5000 PPM$_V$. Moist air can be treated as a mixture of the two real gases, water vapor and dry air. A unit of PPM$_V$ is defined as the ratio of volume of water vapor to that of dry air. Moist air containing water vapor concentrations in the range of 1000 to 5000 PPM$_V$ is equivalent to the saturation temperature in the range of approximately -20 °C to -2 °C at 101325 Pa (1 atm). The correlation of moisture measurements indicated a deviation of approximately ±20% from the overall mean moisture value in this range [1]. However, the existing correlation data and test methods are not sufficient to assure accurate and reliable analyses of moisture content in small packages with volumes on the order of 0.01 cm^3 or less. The recent trend towards manufacture of smaller plastic packages for almost every type of integrated circuit housing implies that the following areas are the most important for research: (1) establishment of a suitable moisture standard in the range 1000 to 5000 PPM,; (2) determination of the upper limit for acceptable moisture level in plastic packages from extensive laboratory correlation experiments; (3) effects of moisture absorption/desorption phenomena associated with mechanical, electrical, and thermal properties of

thermosets for packaging materials; (4) new techniques for measurement and control of moisture in microelectronic packages.

All of the above mentioned research areas involve studies of the thermodynamic properties of moist air. The purpose of this work is, therefore, to provide thermodynamic property values for water vapor density, enthalpy, entropy, and Gibbs free energy associated with moist air in a saturated state containing 1000 to 5000 PPM_V of water vapor. The virial equation state of moist air [2,3,4] is solved to determine water vapor density. Thermodynamic functions of molar enthalpy and entropy are derived in terms of water vapor density, mole fraction of water vapor, mole fraction of dry air, the second virial coefficient, saturation temperature and total pressure. The Gibbs free energy is then calculated from the temperature, enthalpy, and entropy.

2. THE VIRIAL EQUATION OF STATE

One of the most commonly used equations of state for moist air is a power series expression in terms of molar volume V_m of the mixture, as follows:

$$\frac{PV_m}{RT} = 1 + \frac{B_m(T)}{V_m} + \frac{C_m(T)}{V_m^2} + \cdots \tag{1}$$

where P is the total pressure, R is the universal gas constant, T is the absolute thermodynamic temperature, $B_m(T)$ is the second virial coefficient of the mixture, and $C_m(T)$ is the third virial coefficient of the mixture. The terms involving the third virial coefficient are negligible in comparison with the terms containing the second virial coefficient in the range of pressures from 0 to about one atmosphere and temperatures from about -100 °C to about 60 °C [2,3,4]. According to thermodynamics [5] and statistical mechanics [6], the appropriate functional equation relating the interactions of the molecules of dry air and water vapor can be defined as follows:

$$B_m(T) = X_{as}^2 B_{aa} + 2X_{as}X_{ws}B_{aw} + X_{ws}^2 B_{ww} \tag{2}$$

where

X_{as}	=	the mole fraction of dry air in the saturated moist air
X_{ws}	=	the mole fraction of water vapor in the saturated moist air
B_{aa}	=	the second virial coefficient pertaining to interactions between two dry air molecules
B_{ww}	=	the second virial coefficient pertaining to interactions between two water molecules
B_{aw}	=	the second cross-virial coefficient pertaining to interactions between one dry air and one water molecule

The coefficients B_{aa}, B_{aw}, and B_{ww} are given by the following expressions [4]:

$$B_{aa}(T) = 0.349568 \times 10^2 - 0.668772 \times 10^4/T - 0.210141 \times 10^7/T^2 \\ + 0.924746 \times 10^8/T^3, \; cm^3/mol \tag{3}$$

$$B_{aw}(T) = 0.32366097 \times 10^2 - 0.141138 \times 10^5/T - 0.1244535 \times 10^7/T^2 \\ - 0.2348789 \times 10^{10}/T^4, \; cm^3/mol \tag{4}$$

$$B_{ww}(T) = RT(0.70 \times 10^{-8} - 0.147184 \times 10^{-8}e^{1734.29/T}), \; cm^3/mol \tag{5}$$

The mole fraction of water vapor X_{ws} and of dry air X_{as} for moist air at a given pressure P and temperature T are given by the equations, as follows:

$$X_{wt} = f(P,T) e_s(T)/P \tag{6}$$

$$X_{as} = 1 - X_{wt} = \frac{P - f(P,T) e_s(T)}{P} \tag{7}$$

where $f(P,T)$ is the enhancement factor [7,8] and $e_s(T)$ is the saturation water vapor pressure either with respect to water or ice [9,10]. The values of saturation water vapor pressure given by the formulation in [9] agree with those in steam tables [11]. In this work functional equations for $f(P,T)$ and $e_s(T)$ in references [8,10] are used for calculations in Eqs. (6) and (7).

The current NIST humidity calibration standard employs functional equations of enhancement factor and saturation water vapor pressure to calculate values of humidity units such as dew/frost-point and relative humidity in the NIST two-pressure humidity generator [12]. However, the temperature dependence of the enhancement factor is expressed in terms of the International Practical Temperature Scale of 1968 (IPTS-68), as indicated below [8]:

$$f(P,t_{68}) = \exp\left\{ \alpha(t_{68})\left[1 - \frac{e_s(t_{68})}{P} \right] + \beta(t_{68})\left[\frac{P}{e_s(t_{68})} - 1 \right] \right\} \tag{8}$$

where $\alpha(t_{68})$, $\beta(t_{68})$, and $e_s(t_{68})$ are functions of temperature on IPTS-68 and t_{68} is in degrees Celsius. To obtain $f(P,t_{90})$ based on the International Temperature Scale of 1990 (ITS-90) using Equation (8), we need to convert $\alpha(t_{68})$, $\beta(t_{68})$, and $e_s(t_{68})$ to $\alpha(t_{90})$, $\beta(t_{90})$, and $e_s(t_{90})$, respectively. Since the constant coefficients [8,10] associated with $\alpha(t_{68})$, $\beta(t_{68})$, and $e_s(t_{68})$ are based on IPTS-68, one can not merely replace t_{68} by t_{90} for calculating these functional values using the same constant coefficients. The functions $\alpha(t_{90})$, $\beta(t_{90})$, and $e_s(t_{90})$ can be expressed as a function of t_{68} using a Taylor's series expansion truncated after the second order term. We obtain the following equations:

$$\alpha(t_{90}) = \alpha(t_{68}) + \frac{\partial \alpha}{\partial t}\Big|_{68}(t_{90} - t_{68}) + \frac{1}{2}\frac{\partial^2 \alpha}{\partial t^2}\Big|_{68}(t_{90} - t_{68})^2 \tag{9}$$

$$\beta(t_{90}) = \beta(t_{68})(1 + \eta) \tag{10}$$

in which

$$\eta = \frac{1}{\beta(t_{68})}\frac{\partial \beta}{\partial t}\Big|_{68}(t_{90} - t_{68}) + \frac{1}{2}\frac{1}{\beta(t_{68})}\frac{\partial^2 \beta}{\partial t^2}\Big|_{68}(t_{90} - t_{68})^2 \tag{11}$$

and

$$e_s(t_{90}) = e_s(t_{68})(1 + \xi) \tag{12}$$

in which

$$\xi \equiv \frac{1}{e_s(t_{68})}\frac{\partial e_s}{\partial t}\Big|_{68}(t_{90} - t_{68}) + \frac{1}{2}\frac{1}{e_s(t_{68})}\frac{\partial^2 e_s}{\partial t^2}\Big|_{68}(t_{90} - t_{68})^2 \tag{13}$$

The equivalent temperatures on IPTS-68 for a given temperature measurement based on ITS-90 are documented in [13].

In order to compute the thermodynamic properties associated with moist air, it is necessary to make use of the Eqs. (6) and (7). The values of the mole fraction of water vapor and of dry air in moist air can

be calculated when the pressure P and the temperature t_{90} of the moist air are given, provided that the corresponding values of the function $f(P, t_{90})$ are known. Since ITS-90 was designed to accurately represent the Thermodynamic Temperature Scale (TTS), the ITS-90 temperature is a close approximation of the TTS with no more than 4 mK deviation in the range of interest from -100 to 100 °C for humidity measurements [14]. The water vapor density in saturated moist air is:

$$\rho_w = \frac{18.0152 \, X_{ws}}{V_m} \times 10^6 \quad g/m^3 \tag{14}$$

where V_m is obtained from Equation (1) and X_{ws} is obtained from Equation (6).

Equation (14) is then used with other parameters in the calculations of enthalpy, entropy, and Gibbs free energy associated with moist air.

3. THERMODYNAMIC FUNCTIONS

Letting H and S denote molar enthalpy and molar entropy, respectively, at a given pressure P and temperature T, one can write H = H(S,P), where S and P are independent variables, and the thermodynamic relation:

$$dH = TdS + VdP \tag{15}$$

When the Maxwell's relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \tag{16}$$

is substituted in Equation (15), the molar enthalpy of moist air representing the effects of interactions due to dry air and water molecules is given by [15,16]:

$$H'_m(V_m,T) = PV_m - RT + \int_\infty^{V_m} \left[T\left(\frac{\partial P}{\partial T} \right)_{V_m} - P \right] dV_m \tag{17}$$

On combining Eqs. (1), (2), (14), and (17), the molar enthalpy of moist air in a saturated state H_m can be expressed explicitly in terms of water vapor density ρ_w. In the earlier work [3,4,15,17], the enthalpy was expressed in terms of molar volume. Using Equation (1) truncated after the second term, we obtain

$$H_m = X_{as}\left(\sum_{i=o}^{5} a_i T^i + H'_a \right) + X_{ws}\left(\sum_{i=o}^{5} b_i T^i + H'_w \right)$$
$$+ RT \left[\frac{\rho_w \left(B_m - T\frac{dB_m}{dT} \right)}{18.0152 \, X_{ws}} \right] , \; J/mol \tag{18}$$

where H'_a = -7914.1982 J/mol, H'_w = 35994.17 J/mol, the first summation is the ideal gas (zero-pressure) molar enthalpy of dry air, and the second summation is that of water vapor. The constant coefficients a_i's and b_i's are available in [6]. The constant H'_a makes the molar enthalpy of dry air consistent with the assigned value zero at the reference state T = 273.15 K and P = 101325 Pa (1 atm). The constant H'_w makes the molar enthalpy of saturated liquid water consistent with the assigned value zero at the reference state T = 273.16 K, the triple-point temperature for the pure water substance.

The enthalpy of moist air is equivalent to its total energy. Equation (18) shows that the molar enthalpy of moist air is a function of its temperature; the absolute amount of moisture it contains, namely, water vapor density, and its total pressure. The last term of Equation (18) containing the second virial coefficient and its derivative, at a given temperature, account for the deviation of the moist air from ideal gas enthalpies of water vapor and dry air.

The ideal gas molar entropy of dry air S_a° and of water vapor S_w° at P = 101325 Pa (1 atm) are given by [3,4,15,17]:

$$S_a^\circ = R\ln 101325 + \sum_{i=0}^{4} c_i T^i + c_5 \ln T, \; J/(mol \cdot K) \tag{19}$$

$$S_w^\circ = R\ln 101325 + \sum_{i=0}^{5} d_i T^i + d_6 \ln T, \; J/(mol \cdot K) \tag{20}$$

where the constant coefficients c_i's and d_i's are available in [6].

By virtue of Equation (16), it can be shown that the equation for the molar entropy of moist air S_m in a saturated state is given by [14]:

$$\begin{aligned}
S_m &= X_{as}S_a + X_{ws}S_w + X_{as}R\ln\left(\frac{V_m}{X_{as}RT}\right) \\
&+ X_{ws}R\ln\left(\frac{V_m}{X_{ws}RT}\right) + \int_\infty^{V_m}\left[\left(\frac{\partial P}{\partial T}\right)_{V_m} - \frac{R}{V_m}\right]dV_m
\end{aligned} \tag{21}$$

where S_a and S_w are molar entropy of dry air and of water vapor, respectively. On combining Eqs. (1), (2), (14), and (21), the molar entropy of moist air can be expressed explicitly in terms of water vapor density ρ_w, as follows:

$$\begin{aligned}
S_m &= X_{as}(S_a^\circ + S_a') + X_{ws}(S_w^\circ + S_w') - R\ln(P/101325) \\
&+ X_{as}R\ln\left(\frac{18.0152\,PX_{ws}}{\rho_w RTX_{as}}\right) + X_{ws}R\ln\left(\frac{18.0152\,P}{\rho_w RT}\right) \\
&- R\left[\rho_w\left(B_m + T\frac{dB_m}{dT}\right)/18.0152\,X_{ws}\right], \; J/(mol \cdot K)
\end{aligned} \tag{22}$$

where $S_a' = -196.125454$ J/(mol $\cdot$ K) and $S_w' = -63.31449$ J/(mol $\cdot$ K). The constant S_a' makes the molar entropy of dry air consistent with the assigned value zero at the reference state, T = 273.15 K and P = 101325 Pa (1 atm). The constant S_w' makes the molar entropy of saturated liquid water consistent with the assigned value zero at the reference state T = 273.16 K, the triple-point temperature for the pure water substance.

The molar Gibbs energy, G_m, at a given temperature, T, associated with the moist air in a saturated state can be calculated by the following thermodynamic relation:

$$G_m = H_m - TS_m \tag{23}$$

in which H_m and S_m are obtained by Eqs. (18) and (21), respectively.

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4. RESULTS

Table 1 lists values for ρ_w, H_m, S_m, and G_m calculated at eleven water vapor concentration values. The results quoted in Table 1 were obtained with the aid of a personal computer.

Figures 1 and 2 show that at ambient pressure, 101325 Pa (1 atm), ρ_w, H_m, S_m, and G_m increase in magnitude as the water vapor concentration increases. G_m, however, reaches a maximum value of approximately -6.0 J/mol at approximately 3700 PPM_V. It then decreases as the water vapor concentration increases to above 5000 PPM_V. A linear relationship is obtained for water vapor density and water vapor concentration as expected.

5. ESTIMATES OF UNCERTAINTY

The estimated uncertainties in the water vapor densities, molar enthalpies, and molar entropies are identical to the those in [4] for the specific enthalpies and specific entropies of moist air per unit mass of dry air. In the range 1000 to 5000 PPM_V water vapor concentration, the estimated maximum relative uncertainties are 0.6 percent for molar enthalpy and 0.1 percent for molar entropy, respectively. The estimated relative uncertainty of G_m is 0.7 percent based on Equation (23).

Since mole fraction of water vapor is related to saturation water vapor pressure through Equation (6), the uncertainty in ρ_w can be estimated to be

$$\frac{\Delta \rho_w}{\rho_w} \simeq \frac{\Delta e_s}{e_s} \tag{24}$$

The relative uncertainty in the saturation water vapor pressure is small, less than 0.1 percent [10], over the saturation temperature range in this work.

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Table 1. Thermodynamic Property Values Calculated at Eleven Selected
Water Vapor Concentrations in PPM$_V$ for Moist Air in a Saturated
State at 101.325 KPa

| t_{90} (°C)	PPM$_V$	H_m J/mol	S_m J/(mol•K)	ρ_w g/m^3	G_m J/mol
-2	5156	172.6876	0.6654	4.16	-7.7356
-4	4354	78.5931	0.3164	3.55	-6.5660
-6	3667	-10.3605	-0.01629	3.01	-6.0086
-8	3081	-94.8460	-0.3347	2.55	-6.1003
-10	2582	-175.4575	-0.6410	2.16	-6.7784
-12	2158	-252.7181	-0.9368	1.82	-8.0728
-14	1799	-327.0879	-1.2238	1.53	-9.9401
-16	1495	-398.9698	-1.5034	1.28	-12.3705
-18	1240	-468.7166	-1.7769	1.07	-15.3406
-20	1025	-536.6356	-2.0454	0.891	-18.8426
-22	844.3	-602.9944	-2.3098	0.740	-22.8881
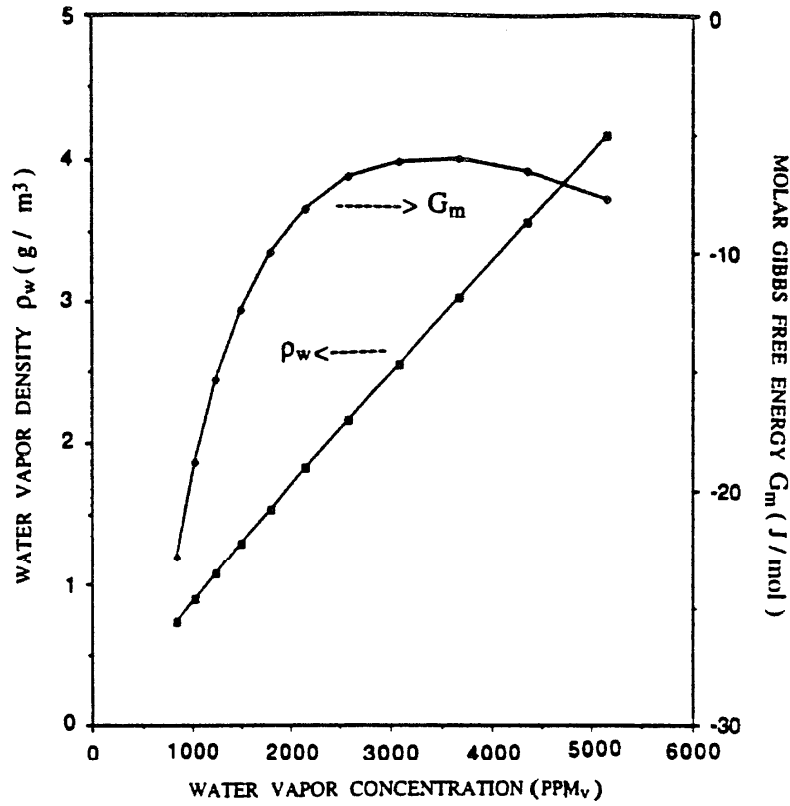
Figure 1. Molar Gibbs free energy G_m and water vapor density ρ_w of moist air in a saturated state at P=101325 Pa (1 atm) as a function of water vapor concentration.
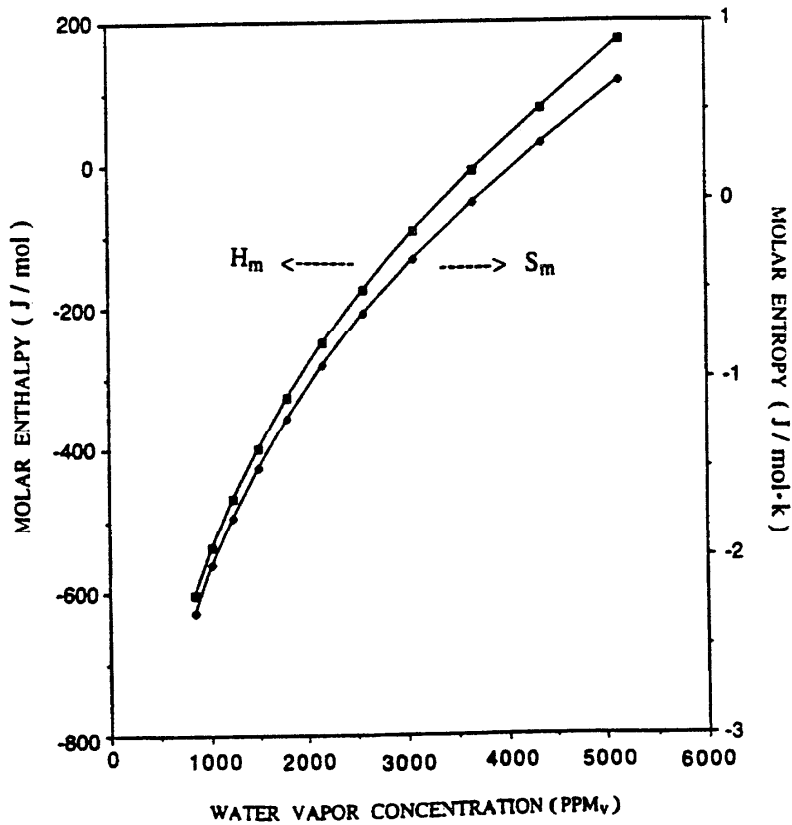

Figure 2. Molar enthalpy H_m and molar entropy S_m of moist air in a saturated state at P=101325 Pa (1 atm) as a function of water vapor concentration.