

Acidic Vapors Above Saturated Salt Solutions Commonly Used for Control of Humidity

ROBERT L. OPILA, JR., MEMBER, IEEE, CHARLES J. WESCHLER, AND RUDOLF SCHUBERT

Abstract—The gaseous transfer from a saturated NaCl solution, of chlorine but not sodium, to copper coupons has been demonstrated in a bell jar that was sealed for nine years. Thermodynamic calculations indicate that the active agent, HCl (g), is in equilibrium with H^+ (aq) and Cl^- (aq) in the saturated salt solution. Auger electron spectroscopy was used to analyze the surface of the copper coupons, and several equivalent monolayers of chlorine were found on the surface. However, the amounts of chlorine found were significantly less than might be expected to be deposited from air in equilibrium with the saturated salt solution. These results are compared with other reported work.

Because laboratory experiments that are designed to accelerate corrosion rates frequently utilize a saturated salt solution to maintain constant relative humidity, the partial pressures of gas phase species in equilibrium with various saturated salt solutions have been calculated.

INTRODUCTION

LABORATORY EXPERIMENTS are frequently designed to accelerate corrosion rates by increasing pollutant concentrations, temperature, or relative humidity (RH). The RH can be controlled by either dynamic or static methods. The former require more labor and equipment (gas cylinders, flow meters, special glassware, etc.). Static control is much simpler; RH is controlled through the use of saturated salt solutions in a sealed chamber [1]–[5]. However, a study by Schubert and Tompkins [6] indicated that components of the salt solutions can be transferred to the surface of metal coupons exposed within such a chamber. This process can further accelerate corrosion and alter surface chemistry in a manner that may not have been anticipated in the original design of the laboratory experiment.

In this paper we will describe an experiment in which copper coupons were placed on wooden blocks in a sealed bell jar containing a saturated NaCl solution. The bell jar remained sealed and undisturbed for slightly more than *nine years*. The saturated NaCl solution maintained a constant humidity and has also been found to be a source of vapor phase HCl. The vapor phase HCl, in turn, interacted with the surface of the copper coupons. The expected concentration of vapor phase HCl within the bell jar was calculated from simple thermodynamic arguments. This calculated concentration was subsequently found to be low, due to the unanticipated release of formic and acetic acids from wood support blocks and subsequent dissolution of these species in the saturated salt solution. The magnitude of this effect has been estimated.

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R. L. Opila, Jr., is with AT&T Bell Laboratories, Murray Hill, NJ 07974.
C. J. Weschler and R. Schubert are with Bell Communications Research, Red Bank, NJ 07701.
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Auger electron spectroscopy was used to analyze the surface of the copper coupons, and several equivalent monolayers of chlorine were found on the surface. However, the amounts of chlorine found were significantly less than might be expected on the basis of HCl released from the saturated salt solution. These results are compared with reported work of others.

Because laboratory experiments that are designed to accelerate corrosion rates frequently utilize a saturated salt solution to maintain constant RH, the partial pressures of gas phase species in equilibrium with various saturated salt solutions have been calculated.

EXPERIMENTAL

Samples

Oxygen-free high conductivity (OFHC) Cu coupons (1 mm thick) were cut to 14 × 14 mm. Samples were cleaned ultrasonically in twice distilled water, followed by 95-percent ethanol. Four coupons were used for the exposure experiment and eight coupons were set aside for future reference.

Chemicals

ACS reagent grade NaCl was used as the solute in the saturated salt solution. The solvent was freshly distilled 18-M Ω water. The solution was prepared in a 250-ml glass beaker, had a final volume of approximately 200 ml, and sufficient water was present to keep the excess NaCl covered with water. Buffers for pH measurements were Fisher Certified, pH 4.00 and pH 7.00.

Equipment and Procedures

The exposure chamber is schematized in Fig. 1. Positioned within a 13-l bell jar were a 250-ml beaker containing the saturated NaCl solution and two kiln-dried wooden blocks. Two copper coupons were placed directly on one of the wooden blocks, and two additional copper coupons rested upon aluminum studs stuck into the other wooden block. Several NaCl crystals were placed on one of the coupons resting on the wooden block and on one of the coupons on an aluminum stud. The remaining two coupons were left bare. On June 7, 1976 the bell jar was sealed with silicone high-vacuum grease and remained undisturbed at ambient temperature (22–25°C) until August, 29, 1985 (over nine years). The initial Auger analyses were performed within hours of opening the chamber.

The Auger investigation utilized a Perkin Elmer—Physical Electronic 595 Scanning Auger Microprobe and spectra were recorded using a 5-kV, 0.5- μ A electron beam rastered over 4

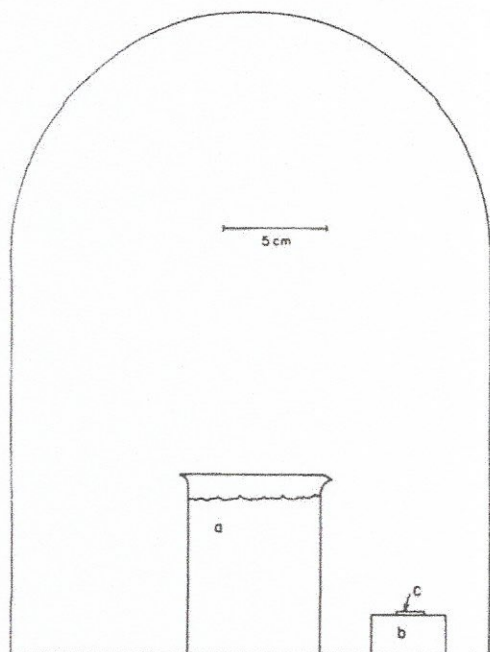


Fig. 1. Schematic drawing of exposure chamber showing relative positions of beaker containing saturated salt solution (a) and wood block (b) supporting a copper coupon (c).

$\times 10^{-4}$ -cm² area. For depth profiling, a 2-kV, 0.2-mA Ar⁺ beam was rastered over 0.10 cm². Under these conditions, the sputtering rate through thermally grown SiO₂ is approximately 50 Å/min.

The pH measurements were made with a Fisher Accumet Model 825 MP pH Meter using two-point standardization with pH 7.00 and pH 4.00 buffers. The electrodes consisted of a universal glass pH electrode and a Calomel reference electrode.

RESULTS

After sitting undisturbed for slightly more than nine years, the bell jar was opened. An odor characteristic of acetic acid emanated from the chamber. More will be said about the source and consequences of the acetic acid below. The copper coupons were visually inspected. The two coupons on which several crystals of NaCl had been placed were severely corroded. Indeed, the surface of these two coupons, including the corrosion products, appeared moist before the bell jar was opened; this was consistent with the presence of salts that deliquesce at 75-percent RH or less. The two bare coupons were not visibly corroded. However, they were slightly darker in appearance than the control coupons that had remained in ambient air during the same time interval. An Auger spectrum of a bare coupon that was exposed in the bell jar is shown in Fig. 2. The major elements detected on this coupon are carbon (C), chlorine (Cl), oxygen (O), and copper (Cu). The large carbon signal is not unusual for surfaces exposed to the ambient environment. A depth profile is shown in Fig. 3, where the Auger intensities of C, Cu, Cl, O, and sulfur (S) peaks are plotted as a function of sputtering time. The depth

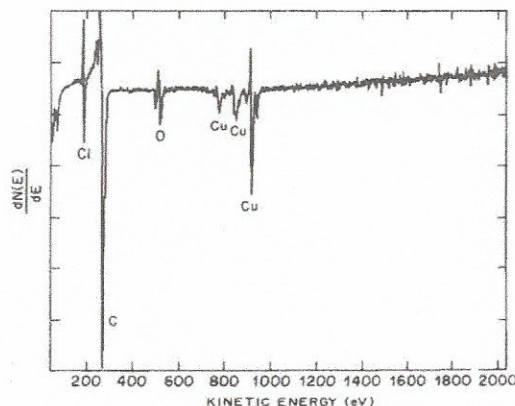


Fig. 2. Auger spectrum of top surface of copper coupon exposed to saturated NaCl solution for nine years.

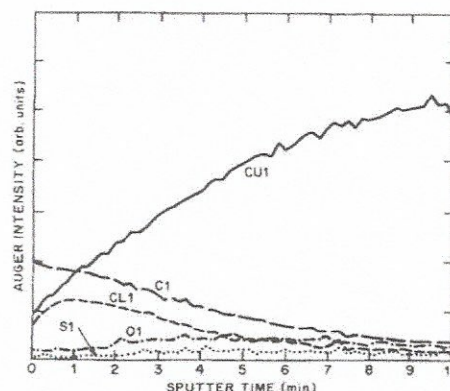


Fig. 3. Elemental depth profile of top surface of copper coupon exposed to saturated NaCl solution for nine years.

profile was interrupted occasionally and the entire Auger spectrum was recorded. Throughout this exercise, *no sodium (Na) was detected*. The intensity of the Auger Cl signal initially increases as a function of sputtering time, reaches a peak, and then decreases. The C Auger intensity was greatest at the surface. The S and O Auger intensities peaked together at longer sputtering times than the Cl peak.

As described in the Experimental Section, eight coupons from the same sheet of OFHC copper were not enclosed in the bell jar, but instead were stored, protected from dust, in ambient air. Several of these coupons were cleaned following the original procedure and inspected by Auger spectroscopy. The Auger spectrum of the surface of one of these coupons is shown in Fig. 4. The C and Cl peaks are less intense and the Cu, O, and S peaks are more intense than the corresponding peaks for the coupons from the bell jar. Na and N are present, but only in small amounts. During depth profiling the C, Cl, O, and S Auger signals decrease monotonically with time. There is significantly less Cl present on the sample stored in room air than on that exposed in the bell jar.

Auger analysis was performed on the reverse side of the bare copper that rested on the wood block (i.e., the side in direct contact with the wood). An Auger spectrum from this surface is displayed in Fig. 5. The C Auger peak dominates the

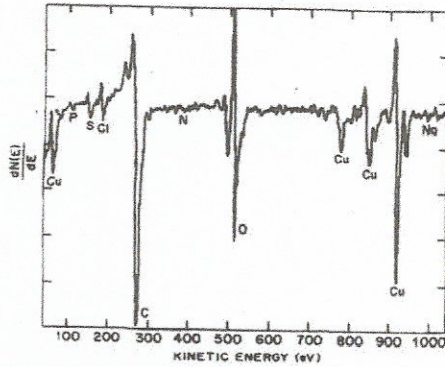


Fig. 4. Auger spectrum of surface of copper coupon not enclosed in the bell jar.

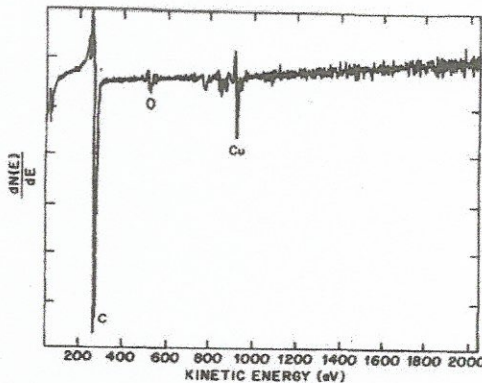


Fig. 5. Auger spectrum of surface of copper coupon that was in direct contact with wood block in the bell jar for nine years.

spectrum, although O and Cu are also evident. The depth profile showed only a monotonic decrease in the C Auger intensity. Some S was detected as sputtering proceeded, but no Cl was seen. The strong C signal may be partially due to acetic and formic acid outgassing from the wood (see below). The lack of a Cl signal on this side (the "wood side"), as contrasted with the significant Cl signal on the reverse side, is evidence that the source of the Cl is not the wood block.

Approximate elemental compositions of the surface films can be determined by dividing the Auger peak-to-peak intensity by the appropriate sensitivity factors, using handbook values [7], and normalizing. Such compositions are summarized in Table I for several areas on each sample after various sputtering times. The approximate atomic concentrations for each coupon confirm that the NaCl solution and not the wood block is the source of the Cl.

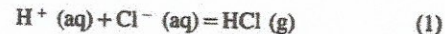
By assuming a sputtering rate equivalent to SiO_2 , (50 Å/min) the depth profile data can be converted to approximate elemental compositions. The amount of Cl in the near-surface region may be roughly estimated by integrating the depth profile. Integration of the Cl depth profile shown in Fig. 3, after converting to atom percent and assuming one monolayer is 5 Å thick, gives 4.5 monolayers of Cl. Taking 2×10^{15} atom/cm²-monolayer, approximately 1×10^{16} atoms of Cl

were transferred to the surface from the salt solution. This estimate is likely to be good to within an order of magnitude.

The presence of Cl without Na on the surface of the bare copper coupons exposed in the bell jar indicates that the Cl was not transferred to the copper surface by surface "creep" of a NaCl solution. Vapor-phase transfer via gas phase HCl is the most probable mechanism. HCl (g) is in equilibrium with the H_3O^+ (aq) and Cl^- (aq) present in the saturated NaCl solution. The equilibrium vapor pressure of HCl over the saturated NaCl solution will depend directly on the concentration of H_3O^+ (i.e., the pH) of the solution. The pH of this solution was measured on two occasions—shortly after the bell jar was first opened and eleven days later (see Experimental). Between the two sets of measurements, the bell jar was sealed. The pH was found to be 3.145 ± 0.003 in the first set of five measurements and 3.152 ± 0.002 in the second set of four measurements. A pH value of 3.15 will be used in subsequent analysis of this system. The reported [8] concentration of chloride ion, $[\text{Cl}^-]$, in a saturated NaCl solution at 25°C is 5.42 molar (M) or 6.15 molal (m). The solution density is 1.1979 g/cm³.

DISCUSSION

The vapor pressure of HCl (g) in equilibrium with a given concentration of H^+ (aq) and Cl^- (aq) can be calculated from thermodynamic considerations. At 298 K and 1 bar, the free energy of formation ΔG_f° of HCl (g) is -95.3 kJ/mol and ΔG_f° of H^+ (aq) + Cl^- (aq) is -131.2 kJ/mol [9]. Consequently, ΔG_r° for the reaction



equals $-95.3 + 131.2 = 35.9$ kJ/mol.

At equilibrium

$$\Delta G_r^\circ = -RT \ln \left[\frac{P_{\text{HCl}}}{a_{\text{H}^+} a_{\text{Cl}^-}} \right] \quad (2)$$

where P is the vapor pressure of HCl in bars, a_{H^+} and a_{Cl^-} are the activities of the hydrogen ion and chloride ion, respectively, T is the temperature (298 K), and R is the gas constant (8.31 J·mol⁻¹K⁻¹).

Rearranging and substituting yields

$$\frac{P_{\text{HCl}}}{a_{\text{H}^+} a_{\text{Cl}^-}} = e^{[-35900/(8.31)(298)]} = 5.07 \times 10^{-7} \text{ bar}. \quad (3)$$

Converting the pressure units from "bar" to "torr" (1 bar = 750 torr) yields

$$\frac{P_{\text{HCl}}}{a_{\text{H}^+} a_{\text{Cl}^-}} = 3.81 \times 10^{-4} \text{ torr}. \quad (4)$$

Equation (4) can be used to calculate the vapor pressure of HCl (g) within the bell jar for the conditions described in the Results Section. The mean activity coefficient of a 6.0-molal solution of NaCl is 0.986 [10]. Hence, the activity of the chloride ion in the saturated salt solution can be approximated by its molality of 6.15 m. The activity of the hydrogen ion, 7.1×10^{-4} , is derived from the saturated salt solution's measured

TABLE I
ELEMENTAL COMPOSITION (ATOM PERCENT)
(Approximate elemental composition as a function of depth for the top and bottom surfaces of a Cu coupon kept in the bell jar chamber for nine years and the composition as a function of depth for an identical coupon after cleaning.)

Sample	Region	Sputtering Time (min)	C	N	O	Na	S	Cl	Cu
Chamber, topside	1	0	62	1	6	1	—	6	25
	2	0	56	1	8	—	—	7	28
	2	1	36	1	8	—	1	11	42
	2	3	19	1	14	—	3	5	58
	2	8	10	—	8	—	2	2	78
	3	0	73	1	4	1	—	3	18
Chamber, bottomside	3	10	11	—	6	—	1	1	82
	1	0	83	1	2	—	—	Tr*	14
	1	25	60	—	3	—	Tr*	—	38
Room	2	0	80	—	2	—	—	—	18
	1	0	54	1	15	1	1	1	28
Room	2	0	53	1	13	1	1	1	30
	2	2	21	1	13	—	2	Tr*	62
	2	4.5	11	1	9	—	1	Tr*	78

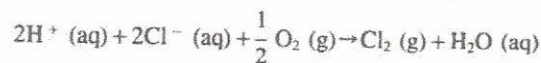
* Tr = Tracc.

pH of 3.15. (The pH of a solution is defined as the negative base 10 logarithm of the hydrogen ion activity.) However, the equation $pH = -\log a_{H^+}$ is employed with the understanding that it is, strictly speaking, a formal relationship, as a_{H^+} is itself undefined—see Harned and Owen [10, p. 443]. Consequently, the vapor pressure of HCl (g), in equilibrium with the pH 3.15 saturated NaCl solution contained within the exposure chamber, was 1.7×10^{-6} torr. This relatively high vapor pressure is directly linked to the unexpectedly low pH of the saturated NaCl solution. Water in equilibrium with air typically has a pH of about 5.6 due to dissolved CO_2 [11]. The high ionic strength of the saturated NaCl solution will increase the pH, but the magnitude of this effect is relatively small, in addition to being in the wrong direction ($\gamma_H \gamma_{OH^-} / a_{H_2O}$ for a 6.15-m NaCl solution equals 2.54 [10], where γ_i is the molal activity coefficient of species i ; this value would correspond to a pH of 7.20 if there were no CO_2 (aq)). Similarly, alkali dissolved from the borosilicate glass of the beaker might also be expected to increase the pH of the solution, but this effect is also in the wrong direction. The measured hydrogen ion activity, two orders of magnitude greater than initially expected, is believed linked to the odor of acetic acid that was noted when the bell jar was opened. The only sources of acetic acid were the three small wood blocks ($2 \times 3.2 \times 8.5$ cm) placed within the bell jar to hold the specimens. Various woods are known to outgas acetic acid [12]–[14]. The type of wood used in this experiment (maple) outgasses both acetic and formic acids, with the concentration of acetic being approximately ten times greater than that of the formic acid [12], [13]. An acetic acid concentration of 2.9×10^{-2} M or a formic acid concentration of 2.9×10^{-3} M is consistent with a pH of 3.15 (K_a (acetic) = 1.76×10^{-5} ; K_a (formic) = 1.77×10^{-4} [15]). Unfortunately, we were not in a position to measure the actual concentration of acetic and formic acid in the saturated salt solution at the time the bell jar was opened. However, given the presence of the wood blocks,

it is not unreasonable that the above concentration would be present during the exposure experiment. For acetic acid, a vapor phase concentration of approximately 8.7×10^{-2} torr would lead to such a solution concentration (ΔG for $CH_3COOH(aq) \rightarrow CH_3COOH(g)$ at 298 K is 22.5 kJ [9]). It is interesting to note that the calculated vapor pressure of HCl (g) within the bell jar, 1.7×10^{-6} torr, is actually higher than reported indoor HCl concentrations and also higher than or comparable to average outdoor concentrations. Rice *et al.* [16] measured mean HCl (g) concentrations between 4.1×10^{-8} and 1.5×10^{-7} torr inside air conditioned buildings at six sites ("urban" and "industrial") across the United States. Matusca *et al.* [17] report outdoor HCl (g) concentrations between 5.1×10^{-8} and 7.1×10^{-7} torr in rural areas, and between 1.0×10^{-7} and 1.5×10^{-6} torr in urban areas. In other words, the equilibrium concentration of HCl (g) above a saturated NaCl solution (pH 3.15), intended to maintain fixed humidity, is greater than that encountered in many real-world applications.

In a hypothetical environmental chamber that contained a saturated sodium chloride solution, in the absence of other factors that influence the solution pH other than atmospheric CO_2 , the pH would be approximately 5.6. In such a case, the vapor pressure of HCl in equilibrium with the solution at 25°C would be approximately 6×10^{-9} torr.

A similar calculation can be performed for the vapor pressure Cl_2 over the salt solution. In this case, the reaction is



and has $\Delta G_r = 25.3$ kJ/mol. This yields Cl_2 vapor pressures of 2.4×10^{-7} torr at pH 3.15, 7.6×10^{-12} torr at pH 5.4, and 4.8×10^{-15} torr at pH = 7, significantly less than the vapor pressure of HCl at these pH's. In fact, the equilibrium vapor pressure of Cl_2 is unlikely to be reached because oxidation by oxygen in acid solutions are kinetically slow unless

appropriate catalysts are present [11]. Given the purity of the H_2O and $NaCl$ that were used in this experiment, the presence of a suitable catalyst is unlikely. Since the vapor pressure of Cl_2 is 0.1 times the vapor pressure of HCl at pH 3.15, we will neglect Cl_2 for the purposes of the following discussion.

Returning to the system that has been the focus of this study, the vapor pressure of HCl is expected to have remained relatively constant over the nine year period after equilibration was achieved (several days). Consequently, the kinetic theory of gases can be used to describe the transport of HCl (g) to the surface of the Cu coupon. An HCl (g) partial pressure of 1.7×10^{-6} torr results in an HCl wall collision rate of approximately $3 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. In nine years there would be approximately 1×10^{23} collisions/ cm^2 with the Cu coupon, yet the Auger analysis indicated the presence of only about 1×10^{16} Cl atoms/ cm^2 . In other words, only one in 10^7 colliding atoms remained on the copper surface. Actually, this description oversimplifies the interaction between HCl (g) and the copper surface. The copper surface was covered with a thin film of adsorbed water. During the nine year exposure, the RH within the bell jar was fixed by the saturated $NaCl$ solution at 75 percent. At 75-percent RH and 30°C , the aqueous film on a gold surface is 30–35 Å thick [18]. Similar studies indicate that approximately ten monolayers of water are present on a copper surface at 75-percent RH [19]. Given that the copper surface is more polar than the gold surface, 30–35 Å can be used as a minimum value for the thickness of the aqueous film on the copper coupons within the bell jar. This aqueous layer is in equilibrium with HCl (g), $HCOOH$ (g), and CH_3COOH (g). Consequently, it contains hydrogen ions, chloride ions, formic and acetic acids, and formate and acetate ions. If the aqueous surface film behaved as bulk water, the solution concentration of these species could be calculated from thermodynamic considerations and the vapor-phase concentrations of the related compounds. However, in such a thin film, solid/liquid and liquid/air interface effects are expected to be strong and to propagate throughout the water layers. According to corrosion literature [20], unless an oxidizing agent is present, copper is expected to display little reactivity under such conditions. Indeed, the amount of chlorine detected on the copper surface may reflect a quantity determined by stability constants for various copper- and chlorine-containing complexes (i.e., values obtained from equilibrium considerations), rather than a quantity determined by irreversible reactions of chloride ions with copper over the entire nine-year period.

However, it should be noted that under similar conditions (vapor pressure of HCl between 1.3×10^{-6} and 3.8×10^{-6} torr) Rice *et al.* [21] report a much greater corrosion rate than we observed in the present study. There are several possible explanations for this: 1) If the rate-determining step in the HCl corrosion of copper is strongly pH -dependent, different pH 's in the aqueous films on the copper surfaces could lead to different corrosion rates. However, available information suggests that the surface pH 's in the two sets of experiments are comparable. 2) Initial corrosion rates on copper are expected to be much greater than final corrosion rates (Graedel *et al.* [22]). However, the small amount of product we observe

does not allow for a large rate even in the initial day of exposure. 3) The work of Rice *et al.* was conducted in a flowing system (50–500 l/min) while the present study considers test coupons in a static system. However, given the small dimensions within the bell jar, it seems unlikely that mass transport limitations would occur. 4) The presence of acetic acid in the "bell jar" experiment may generate a copper acetate film of sufficient thickness to significantly deter HCl/Cu corrosion processes (see, e.g., Tompkins and Allara [23]). The Auger studies (Fig. 3) are inconclusive with regards to the existence of a copper acetate film. The carbon Auger intensity is typical of surfaces exposed to the ambient environment, and the oxygen Auger intensity is not correlated with the carbon Auger intensity as would be expected for an acetate film. However, other work has shown that copper oxalate and formate salts will decompose to CO_2 under electron and ion bombardment, resulting in no detectable carbon Auger signal from these species [24]. Further experiments are planned to elucidate the reasons for the discrepancy in corrosion rate between the present study and that reported by Rice *et al.* [21].

The mechanism described by scenario 4) above is probably operative on the bottom, "wood" side of the coupon. Since the mean free path for air is approximately 6×10^{-6} cm at 760 torr and the surface roughness of the wood blocks was approximately 3×10^{-3} cm, significant amounts of HCl could have been present in the regions between the Cu coupon and the wooden block. Yet negligible amounts of Cl were detected on the bottom side of the Cu coupon. Because of the proximity of the wooden block, a thicker adsorbed film, undoubtedly containing significant amounts of formate and acetate, likely formed on the bottomside of the coupon, and this adsorbed film could inhibit the corrosion of Cu by HCl , as described above.

Nevertheless, the work of Rice *et al.* [21] does demonstrate that low concentrations of HCl , comparable to those that can be generated above saturated salt solutions, have the potential to cause significant amounts of copper corrosion. The concentrations of HCl (g) generated in an environmental chamber containing a saturated $NaCl$ solution can react to an even greater extent with other materials (e.g., aluminum). Furthermore, other saturated salt solutions, commonly used in environmental chambers for the static control of RH, can also generate significant concentrations of potentially corrosive vapors.

Table II lists calculated vapor pressures of gas phase species, mostly acids, in equilibrium with various saturated salt solutions in a closed system at 25°C . The list is by no means exhaustive. However, it does include each of the saturated aqueous salt solutions described in ASTM Standard E 104, "Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions" [1]. The entries in Table II have been calculated using the same approach outlined above to calculate the vapor pressure of HCl (g) in equilibrium with a saturated solution of $NaCl$. Values of ΔG° were derived from the appropriate quantities as tabulated in "The NBS Tables of Chemical Thermodynamic Properties" [9] and the concentrations of the ionic species were taken from "Solubilities of Inorganic and Organic Compounds" [8]

TABLE II
VAPOR PRESSURE ABOVE SATURATED SALT SOLUTIONS
(Calculated equilibrium vapor pressure above saturated salt solutions at pH 7, 5.6, and 3.15, or at the pH of the solution when the salt acts as a buffer.)

Salt	T(°C)	RH	Gas Phase Species	Vapor Pressure (torr) at pH			Vapor Pressure at	
				7	5.6	3.15	pH	(torr)
LiCl·H ₂ O	25	11.1	HCl	5 × 10 ⁻¹⁰	1 × 10 ⁻⁸	4 × 10 ⁻⁶		
K(CH ₃ CO ₂)	25	22.7	CH ₃ CO ₂ H				9.6	3 × 10 ⁻⁶
CaCl ₂ ·H ₂ O	25	28.8	HCl	6 × 10 ⁻¹⁰	2 × 10 ⁻⁸	4 × 10 ⁻⁶		
MgCl ₂ ·6H ₂ O	25	32.8	HCl	5 × 10 ⁻¹⁰	1 × 10 ⁻⁸	3 × 10 ⁻⁶		
NaI	25	38.4	HI	4 × 10 ⁻¹³	1 × 10 ⁻¹¹	3 × 10 ⁻⁹		
K ₂ CO ₃	25	43.2	CO ₂				12.6	5 × 10 ⁻⁴
Ca(NO ₃) ₂ ·4H ₂ O	25	50.5	HNO ₃	3 × 10 ⁻¹⁰	9 × 10 ⁻⁹	2 × 10 ⁻⁶		
Mg(NO ₃) ₂	25	52	HNO ₃	3 × 10 ⁻¹⁰	8 × 10 ⁻⁹	2 × 10 ⁻⁶		
NaBr	25	57.7	HBr	1 × 10 ⁻¹²	3 × 10 ⁻¹¹	7 × 10 ⁻⁹		
Mg(CH ₃ CO ₂) ₂	25	65	CH ₃ CO ₂ H				9.9	6 × 10 ⁻⁶
Na(CH ₃ CO ₂)·3H ₂ O	25	72.6	CH ₃ CO ₂ H				9.7	4 × 10 ⁻⁶
NaNO ₃	25	73.8	HNO ₃	3 × 10 ⁻¹⁰	8 × 10 ⁻⁹	2 × 10 ⁻⁶		
NaCl	25	75.3	HCl	2 × 10 ⁻¹⁰	6 × 10 ⁻⁹	2 × 10 ⁻⁶		
NH ₄ Cl	25	79.3	Cl ₂	5 × 10 ⁻¹⁵	8 × 10 ⁻¹²	2 × 10 ⁻⁷		
			NH ₃				4.2	8 × 10 ⁻⁴
KBr	25	80.7	HBr	6 × 10 ⁻¹³	2 × 10 ⁻¹¹	4 × 10 ⁻⁹	4.2	2 × 10 ⁻⁷
(NH ₄) ₂ SO ₄	25	81.1	NH ₃				5.5	3 × 10 ⁻²
			SO ₃				5.5	6 × 10 ⁻¹²
			H ₂ SO ₄				5.5	5 × 10 ⁻²⁴
KCl	25	84.3	HCl	2 × 10 ⁻¹⁰	5 × 10 ⁻⁹	1 × 10 ⁻⁶		
Na ₂ CO ₃	24.5	87	CO ₂				12.4	5 × 10 ⁻⁴
BaCl ₂ ·H ₂ O	25	90	HCl	1 × 10 ⁻¹⁰	3 × 10 ⁻⁹	7 × 10 ⁻⁷		
KNO ₃	25	92.5	HNO ₃	1 × 10 ⁻¹⁰	3 × 10 ⁻⁹	8 × 10 ⁻⁷		
Na ₂ SO ₄	20	95	SO ₂				10.8	4 × 10 ⁻¹⁰
K ₂ SO ₄	25	97.3	SO ₃				8.0	7 × 10 ⁻¹⁸
			H ₂ SO ₄				8.0	6 × 10 ⁻³⁰

Bowden-32%
32%

72% 75% 78%
69% 65% 67%
59% 65% 67% 84%

72%

21

Vapor pressures of the gas phase species have been calculated for three different hydrogen ion activities: pH 7, pH 5.6, and pH 3.15. At the hydrogen ion activity most likely to exist in simple exposure studies, pH 5.6, numerous saturated salt solutions generate HCl (g) and HNO₃ (g) concentrations on the order of 10⁻⁸ to 10⁻⁹ torr; HBr (g) concentrations are typically two orders of magnitude smaller (see Table II). Certain saturated solutions, prepared from the salt of a weak acid or a weak base, fix the hydrogen ion activity. The vapor pressure of the corresponding gas phase species is also fixed. For acetate salts, the vapor-phase concentrations of acetic acid are greater than 10⁻⁶ torr. In the case of ammonium salts, the vapor pressure of NH₃ (g) above the saturated solution can be very high (e.g., 3 × 10⁻² torr for (NH₄)₂SO₄ and 8 × 10⁻⁴ torr for NH₄Cl). In many studies such concentrations are sufficiently high for these species to become important components of the exposure experiment.

CONCLUSIONS

We have demonstrated the gaseous transfer of Cl from a saturated NaCl solution to nearby Cu surfaces. Thermodynamic calculations indicate that the active agent is HCl (g), in equilibrium with H⁺ (aq) and Cl⁻ (aq) in the saturated salt solution. Investigators must be aware of the vapor pressures of gas phase species in equilibrium with various saturated salt solutions. However, the authors are unaware of any discussion of this point in the literature that describes such solutions for

maintaining constant humidity. We have presented partial pressures of corrosive gases in equilibrium with a variety of saturated salt solutions (Table II). This table is representative, not comprehensive. However, ΔG_f^o values and salt solubilities are published [8], [9] that permit calculations, similar to those used to prepare Table II, for any of the salt solutions commonly used for the control of humidity. Adequate knowledge of the vapor-phase chemicals in an exposure experiment requires that such calculations be made, or referred to, any time salt solutions are used for the static control of humidity in an enclosed air space.

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