

Moisture Ingress into Nonhermetic Enclosures and Packages. A Quasi-Steady State Model for Diffusion and Attenuation of Ambient Humidity Variations

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ABSTRACT

In this paper the rate of moisture ingress into enclosures was studied theoretically and experimentally. A simple quasi - steady state (QSS) model was developed enabling one to calculate easily time constants for moisture diffusion through plastic walls, rubber gaskets and openings. The characteristic time constant is $\tau = VL/AP + L^2/2D$ where P is permeability, D - diffusion constant, V - volume of the enclosure, L - wall thickness and A - surface area. The model clarifies the relative importance of moisture permeability vs. diffusion constant of wall materials and is applicable to both large enclosures and microelectronic packages. For thin and/or non-absorbing walls the first term (a function of P) predominates while with thick and/or absorbing walls the second term (which depends on D) prevails. For openings, $\tau = VL/AD$. It was shown that the QSS model is practically equivalent to but simpler than full transient solutions of the Fick's second law. The attenuation of variations of atmospheric humidity by packaging was also modeled with the QSS model. The inside air humidity changes with the same frequency as the ambient but its amplitude is attenuated by a factor $f = \cos\phi = 1/(1 + \omega^2\tau^2)^{1/2}$ and is phase shifted by an angle $\phi = \arccos [1/(1 + \omega^2\tau^2)^{1/2}]$ where ω is the angular frequency of humidity changes. Therefore the protective value of packaging will be different in different geographical areas.

I. INTRODUCTION

The pivotal role atmospheric water plays in the functionality, reliability and durability of electronic devices is a well established fact and a large effort is devoted throughout the industry to either prevention of the presence of water in the

instrumentation or its desensitization to water effects (e.g., corrosion protection). There is a multitude of paths moisture can penetrate into and out of the building block, e.g., through permeable walls, and gasket material (dealt with in this paper) as well as through cracks, pinhole and other openings both via diffusion and through the process of the air exchange caused by thermal expansion, i.e., breathing. Additionally, for outdoor equipment the rate and direction of moisture penetration will depend on a multitude of ambient conditions, viz., relative and absolute humidity, temperature, air mass movement and frequency of climatic cycles. Finally, the material from which the equipment is made will govern the tendency to retain, release and precipitate moisture in different conditions.

The purpose of this paper is to achieve understanding of factors governing kinetics of moisture diffusion into enclosures in terms of building materials properties and ambient conditions. The presented results are part of basic research done at BNR which is being utilized in the development of Northern Telecom products.

An important factor for reliability is the relative importance of the absolute humidity (AH) vs. relative humidity (RH). The majority of failure mechanisms (e.g., those related to electrochemical corrosion) are highly dependent on the presence of a liquid water layer of a certain thickness on the surface and, accordingly, they usually exhibit a threshold RH value. Leakage currents on triple track testers are known to have different activation energies below and above a certain RH [1] pointing out to a change in the mechanism of conduction. There is no general agreement as to the threshold thickness required for ionic conductivity. Values of 8 to 10 monolayers are frequently assumed to be necessary but as few as 3 monolayers are sometimes claimed to be sufficient.

The relationship between the thickness of the surface adsorbed water layer and relative humidity

can be best rationalized in terms of the Brunauer Emmett-Teller (BET) model of adsorption of vapors [2-4]. In the BET model the first layer of a water is bound to the surface with energy E_0 . Subsequent layers of water molecules bind to the underlying molecules with the energy $E_1 = E_2 = E_3 = \dots = E$ which is identical to the energy of evaporation. Arguments based both on kinetics and on statistical thermodynamics [2] lead to the expression (1) for the average number of monolayers on the surface N .

$$N = \frac{R(p/p_0)}{(1 - p/p_0)[1 + (R - 1)p/p_0]} \quad (1)$$

where $R = \exp [(E_0 - E)/RT]$ and p/p_0 is the ratio of the vapour pressure to the vapour pressure in the state of equilibrium with the liquid phase (saturation), i.e., the relative humidity. It can be estimated from Eqn. (1) that with moderately and strongly hydrophilic surfaces ($E_0 \geq E$) the air humidity threshold for failure (i.e., RH causing formation 4-8 monolayers of liquid water) is around 70-90%, in agreement with reliability studies, while hydrophobic materials ($E_0 < E$) will resist formation of thicker water layers up to very high humidities.

Formation of liquid water layers may be also triggered by the presence of water soluble impurities which are usually, but not necessarily, ionic [5]. When the relative humidity exceeds a critical value RH_{crit} which corresponds to the water chemical potential of the saturated solution, water will condense until an equilibrium is established. Thus the presence of a soluble impurity may cause leakage current and/or corrosion at relatively low humidities, e.g., with calcium chloride impurity above 29% and with lithium chloride as low as 11% [5].

While the *reliability of equipment is related to relative humidity, the process of moisture diffusion through materials is related to the absolute humidity*, i.e., moisture concentration in air, as expressed by Fick's diffusion laws [6] which deal with concentration gradients, Eqns. (2) and (3)

$$\text{Fick's first law:} \quad F = -D \frac{\partial c}{\partial x} \quad (2)$$

$$\text{Fick's second law:} \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

where c is water concentration in the material or absolute humidity and F is defined as amount of

substance being transported through unit crosssection per unit of time, i.e., $F = Q/At$.

As RH is related to AH through an exponential function of temperature, $RH = (AH) A \exp (B/T)$, temperature and especially temperature changes will strongly influence reliability issues.

Despite the importance of the moisture diffusion into electronic equipment from the reliability point of view, there is some confusion as to the *relative roles of the diffusion constant, D and permeability P* (defined as the product of D and solubility partition coefficient K) in different situations. The permeabilities are (correctly) usually used in steady state conditions, e.g., when water is consumed inside the enclosure while diffusion coefficients are (also correctly) used with purely transient situations, e.g., when studying water sorption into plastic microelectronic packages. The difficulty arises in the intermediate situations when the cavity in the enclosure is comparable in terms of geometrical dimensions and moisture capacity to the enclosure walls. Some materials, e.g., silicones, owe their high moisture permeability to their large diffusion coefficients at very low water solubility, other, e.g., nylons, to high solubility at relatively low diffusion coefficients. Similar situation may arise when comparing two materials of low permeability. The protective function of wall materials will be different with different equipment design and it is important to achieve a clear understanding of these factors. In this paper a relatively simple, so called *quasi - steady state* (QSS) model will be presented which is equivalent to a full transient model resulting from the solution of differential equations of the Fick's second law for the general case of an enclosure with a finite size cavity which will be also discussed.

Besides diffusion through the packaging material there are other possible routes of moisture ingress into an enclosure and most of them are related to the presence of openings in the walls which may be both of intentional (e.g., vents) or non-intentional (e.g., cracks, pinholes or other imperfections). With the exception of very narrow openings where either the viscous flow regime or Knudsen flow regime may apply [7] which is mostly of concern in hermetic packaging, moisture ingress will follow regular diffusion equations through air in these openings.

As it will be demonstrated, the time constants for moisture ingress into packages and enclosures are relatively short and sooner or later the inside humidity will reach the ambient humidity value, with τ ranging usually from minutes at worst to

weeks at best. Thus with constant ambient humidity non-hermetic packaging by itself does not provide any significant protection from moisture. However, the ambient humidity is not constant and that's where the enclosures can play a role. An important function of moisture protection by packaging materials is attenuation of the ever changing ambient conditions.

A model describing relationship between the characteristic moisture ingress time constants, frequency of ambient humidity changes and the attenuation factor will be described.

II. ANALYSIS

1. Enclosures with desiccant. Steady state.

Let us consider a container with one plastic wall of thickness L whose water diffusion coefficient is D (see Fig. 1). If a sufficient amount of a fast absorbing desiccant is placed inside the container, the moisture concentration c_i in the air inside the box will be constant (and close to zero). The ambient moisture concentration c_a is also constant and thus a steady state concentration profile in the wall will be established. Thus in the diffusive wall (membrane)

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} = 0 \text{ and therefore } \frac{\partial c}{\partial x} = \text{const} = \frac{c_a - c_i}{L},$$

in other words Fick's first law applies here.

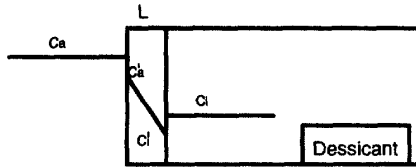


Fig. 1. Diffusion into an enclosure with desiccant

On both surfaces of the wall a fast equilibrium between water concentration in air and water concentration in the plastic is established according to Henry's law with a partition coefficient or equilibrium constant K such that $K = c'_i/c_i = c'_a/c_a$. Thus from Fick's first law the flow

$$F = D \frac{c'_a - c'_i}{L} = KD \frac{c_a - c_i}{L} = P \frac{c_a - c_i}{L} \quad (4)$$

where $P \equiv KD$ is the permeability [coefficient]. The somewhat confusing issue of units of permeability is dealt with in the Appendix.

Permeability is the most extensively determined and tabulated transport property of polymeric materials [8-10] and we owe this fact mostly to the food industry. In literature search, it is much easier to find a permeability value of a polymer than its diffusion coefficient because most determinations have been made in steady state experiments and such experiments do not allow one to separate P into D and K . The total amount of water Q diffusing through a membrane of surface A into an enclosure in steady state conditions over time t may be calculated as

$$Q = PA \frac{c_a - c_i}{L} t \quad \text{or} \quad Q = PA \frac{c_a}{L} t \quad (5)$$

for a good desiccant ($c_i = 0$). This can be utilized to calculate the lifetime of a desiccant in the enclosure.

Steady state diffusion has its electrical analogue in charging of a battery from a constant voltage source. As long as the battery's (desiccant's) capacity has not been exhausted, there is a constant potential difference (moisture concentration gradient) and we have a constant current (moisture flow). The product LAP is here a counterpart of the electrical resistance and P is the analogue of electrical conductivity.

2. Enclosures with no desiccant. Quasi - steady state approximation with non-absorbing walls.

Let us now remove the desiccant from the discussed enclosure. Now, the inside humidity concentration will be gradually increasing and thus there is no constant concentration gradient. Thus, in principle, Fick's first law will not apply and we should be solving the more general Fick's second law equation, eqn. (3). However, if we assume that the diffusive wall (membrane) is so thin that the distribution of water within it may be still considered approximately linear (although changing in time, see Fig. 2), we may still be able to use Fick's first law in order to follow the humidity concentration changes in time.

The applicability of this quasi - steady state approach depends on the given system, especially the membrane thickness. We have a right to expect that it will fail for thick and absorbing walls. Despite the error it introduces, the approach will enable us to understand phenomena related to the way the internal air humidity follows the ambient humidity and will let us introduce the notion of the time constant for moisture ingress.

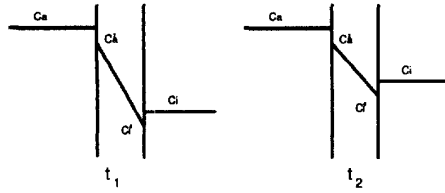


Fig. 2. Moisture concentration distribution in quasi - steady state approximation

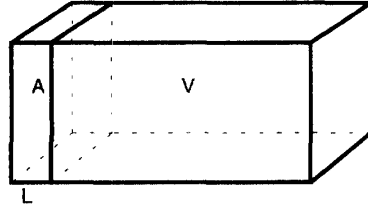


Fig. 3. An enclosure with a permeable wall to illustrate the quasi - steady state approach

Let us consider a container of volume V with a plastic wall of thickness L and surface area A in the ambient air of constant moisture concentration c_a (Fig. 3). Let us assume that initially there is no moisture in the container ($c_{oi} = 0$). The change of the internal moisture concentration c_i depends on the flow of moisture through the wall as follows:

$$\frac{dc_i}{dt} = \frac{A}{V} F \quad (6)$$

Since
$$F = P \frac{c_a - c_i}{L} \quad (7)$$

we have the following differential equation for the internal humidity concentration.

$$\frac{dc_i}{dt} = \frac{AP}{VL} (c_a - c_i) \quad (8)$$

The solution of this equation for the initial conditions of $c_i = 0$ at $t = 0$ is given by Eqn. (9):

$$c_i = c_a \left[1 - \exp\left(-\frac{AP}{VL} t\right) \right] \quad (9a)$$

Eqn.(9) describes a typical exponential relaxation process with the time constant (or relaxation constant) τ defined as

$$\tau \equiv VL/AP \quad (10)$$

Thus defined time constant is the time in which the inside air humidity will reach the fraction $(1 - 1/e) \approx 0.63$ of the ambient value. In a more familiar form

$$c_i = c_a \left[1 - \exp\left(-t/\tau\right) \right] \quad (9b)$$

The moisture ingress into the container described by Eqns. (9) is shown as the first fragment of the c_i curve in Fig. 4.

The electrical analogue of the described process is charging of a condenser upon closing of a circuit with a constant voltage source. In this case, V is a counterpart of the circuit capacitance and L/AP is, again, equivalent to its ohmic resistance.

An important difference between the steady state and the pseudo-steady state diffusion is the fact that in the latter the rate of the moisture ingress depends on the volume of the container and in the former it does not.

When the initial concentration of moisture in the container is different than zero, the initial condition is $c_i = c_{oi}$ for $t = 0$ and the solution of Eqn. (8) is

$$c_i = c_a - (c_a - c_{oi}) \exp\left(-t/\tau\right) \quad (11)$$

This is shown in Fig. 4 as different fragments of the c_i curve.

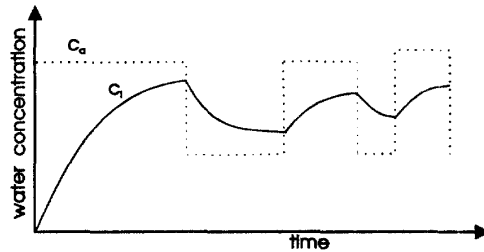


Fig. 4. Air humidity inside the enclosure follows the changes in ambient humidity.

3. Enclosures with no desiccant. Quasi - steady state approximation with absorbing walls.

The described above model breaks down with thicker walls and/or ones made of a more hydrophilic material. Here, water absorption into the wall material has to be taken into account. The concentration of water at the external wall surface

is Kc_a and on the internal one Kc_i . Assuming a linear distribution of moisture in the wall the average water concentration in the material is $K(c_a + c_i)/2$ and the total water amount in the wall is $K(c_a + c_i)/2$. As c_a is constant, any increase of c_i , dc_i will lead to the accompanying increase of moisture in the wall by $KV_{wall}dc_i/2$.

In the balance, a part of permeating water is used up to increase the moisture concentration in inside air and another part to increase amount of moisture in the wall.

Thus, the differential equation (6) will be modified here to reflect the wall effect [Eqn (12)]:

$$\frac{dc_i}{dt} = \frac{AP}{VL + V_{wall}LK/2} (c_a - c_i) \quad (12)$$

Upon integration a relaxation type equation identical to either Eqn. (9) or, depending on the initial conditions, Eqn (11) is obtained with the time constant of

$$\tau = \frac{VL + V_{wall}LK/2}{AP} \quad \text{i.e.,} \quad \tau = \frac{VL}{AP} + \frac{L^2}{2D} \quad (13)$$

since $V_{wall} = AL$ and $P = KD$. Eqn. (13) is a generalized version of Eqn. (10) defining the moisture diffusion time constant which it replaces.

Interesting conclusions can be drawn by analyzing Eqn. (13). We can see that for systems characterized by a large cavity volume V and/or thin walls and/or small crosssection area the first term predominates and the permeability is the most important wall material property. This is a situation encountered with thin membranes (e.g., in food packaging), non-absorbing walls (e.g. ones made of Teflon) and metal boxes with relatively small amount of rubber gasket material (small A). For systems with a negligible cavity volume (like in microelectronic packages) and/or thick and/or absorbing walls the second term predominates and the relevant wall material property is its diffusion coefficient. In this situation the time constant will not depend on the container's volume or wall surface area.

Eqn (13) additionally suggests that with thick and/or absorbing walls replacing some (even most) walls with metal or ceramic will not increase the moisture diffusion time constant significantly, e.g. as much water will diffuse into an all nylon container as into one made with 5 metal walls and only one wall made of nylon. Only when the amount of plastic becomes really small

(i.e., comparable with that in a gasket) the time constant will increase significantly. Similarly, a microchip package with only one plastic wall will have the same moisture ingress time constant as an all plastic package.

4. Relationship to full transient models

The quasi - steady state model presented above is, of course, a simplification of a transient problem. It is important to know how justified we are when using it. Let us thus consider again moisture diffusion into the container shown in Fig. 3. This time, however, we do not assume the quasi - steady state approximation. At time t there is a certain distribution of moisture within the wall. The gas phase inside the container is in equilibrium with the internal wall surface with the constant K and the same holds for the ambient air - the external wall surface. This is the most general case considered in the context of packaging: *the diffusion into a container with a finite volume*. Our model should reduce either to the "diffusion into a slab" when the internal volume of the container is very small when compared with the volume of the wall (situation encountered in microelectronic packages) or to the flow through membrane in when the internal volume is extremely large (situation equivalent to container with desiccant).

Assuming that in the beginning there was no humidity in the box the initial and boundary conditions for this case (in terms of the nomenclature of Fig. 2.) are as follows:

$c = 0$ for $0 < x < L$ at $t = 0$, $c = c_a' = Kc_a$ for $x = 0$ at $t > 0$,

and additionally there is a flow continuity condition at surface $x = L$, viz.,

$$D \frac{\partial c}{\partial x} + \frac{V}{AK} \frac{\partial c}{\partial t} = 0 \quad \text{for } x = L \text{ at } t > 0$$

The solution for the analogous heat conduction problem of a slab in contact with a perfect conductor or a well stirred fluid was given by Carslaw and Jaeger [11] and adopted to the diffusion problem by Paul and Benedetto [12] to yield Eqn. (14).

$$\frac{c_i}{c_a} = \frac{c_i}{c_a} = 1 - \sum_k \frac{2(\beta_k^2 + \eta^2) \sin \beta_k}{\beta_k(\beta_k^2 + \eta^2 + \eta)} \exp\left(\frac{-\beta_k^2 Dt}{L^2}\right) \quad (14)$$

where $\eta \equiv LAK/V = KV_{wall}/V$ and β_k are the roots (eigenvalues) of the equation $f \tan f = \eta$. Values of

β_k are tabulated in the literature [6a,11]. [All the equations, definitions and boundary conditions are modified here to reflect our preferred unit systems in which P and D have the same dimensions (see Appendix)]:

For very large V , $\eta = 0$, $\beta_k = k\pi$ and it can be shown [12] that the situation reduces to the flow through membrane, i.e. the situation as shown in Fig. 1 for the initial stage when the steady state described above has not yet been established. For the appropriate initial and boundary conditions Barrer [6a,12] arrived at the expression (15) for the amount of moisture passing through the internal wall surface ($x = L$), i. e., entering the enclosure over time t .

$$Q_t = \frac{DAc_a}{L} \left(t - \frac{L^2}{6D} \right) - \frac{2ALc_a}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) \quad (15)$$

Eqn. (15) is the basis of the so called "time lag" method of determining transport parameters which allow separation of P into D and K [6].

Differentiating Eqn. (15) with respect to time gives us the rate of the moisture ingress, dQ/dt

$$\frac{dQ}{dt} = \frac{DAc_a}{L} + \frac{2DAc_a}{L} \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) \quad (16a)$$

For very small values of L the exponential term in Eqn. (16a) will be vanishingly small and

$$\frac{dQ}{dt} = \frac{DAc_a}{L} \quad (16b)$$

Since $dQ = Vdc_a$, Eqn.(16b) is equivalent to Eqn. (8) (for the zero initial inside humidity, $c_i = 0$) and thus the process of moisture ingress will be described by Eqn. (9) with the time constant of $\tau = VL/AP$.

Thus we have shown that the QSS model with non-absorbing walls, i.e., when the first term of Eqn. (13) defines the τ approximates the full transient model for large V .

In the other extreme, i.e., for very small V (i.e., $V \rightarrow 0$), $\eta = \infty$ and $\beta_k = (k+1/2)\pi$ and the problem reduces to the problem of diffusion into a slab, i.e., Eqn. (14) reduces to Eqn. (17) describing the moisture concentration in the cavity (i.e. for $x = L$) which can be also derived by solving Fick's second law for the initial and boundary conditions appropriate for this situation [6a]:

$$\frac{c_i}{c_a} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{D(2n+1)^2\pi^2 t}{4L^2}\right) \quad (17)$$

Eqn. (17) describes water concentration in an infinitesimally small cavity in the middle of a slab of half-thickness L placed in air with ambient humidity c_a and is applicable to moisture diffusion into plastic chip packages when the moisture concentration at the chip surface is of interest.

Although Eqn. (17) is a series of exponential rather than a single exponential, we can define a "time constant" as the time after which water at the polymer - substrate interface will achieve $1-1/e$ (approximately = 0.63) of the ambient value (i.e., $c_i/c_a = 1 - 1/e$). From Eqn. (17) we find that it will happen when $Dt/L^2 = 0.505$. Thus the "time constant" can be estimated as

$$\tau = 0.505 L^2/D$$

Now, we know that in the quasi - steady state model with absorbing walls the second term of the equation (13) for the time constant predominates when $V \rightarrow 0$ and

$$\tau = L^2/2D$$

Those two expression for time constants are identical for all practical purposes. Both the transient and the quasi - steady state approach give us the same important result that for the thick and/or absorbing walls the time constant is proportional to the square of the wall thickness

Thus, despite its simplicity, the QSS approach seems to approximate quite well the full transient model both with the thin and the thick wall extremes.

5. Moisture diffusion through an opening

For an opening fulfilling criterion 3a, all the diffusion equations will apply. There is only one minor difference when compared with diffusion through a plastic wall. The partition coefficient $K = 1$ because we are dealing here with only one phase (see Fig. 5). In other words permeability is equal to the diffusion coefficient ($P = KD = D$), as long as we use proper units of permeability (see Appendix in paper [1]). The diffusion coefficient of water in air is $0.24 \text{ cm}^2/\text{s}$ [15]

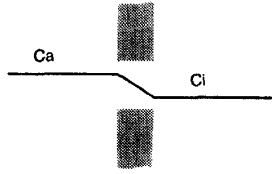


Fig. 5. Moisture diffusion through a pinhole in the wall. The concentration profile.

Thus for the case of a *container with desiccant*, i.e., when conditions for steady state diffusion are fulfilled (constant concentration gradient) the amount of water diffusing through a crack of area A in the wall of thickness L over time t is described by Eqn (18)

$$Q = DA \frac{C_a - C_i}{L} t \quad (18)$$

When the desiccant is removed from the enclosure, we have the situation for which the quasi - steady state approximation applies and the moisture concentration inside the enclosure will be described by Eqn. (11) or, when the initial humidity in the container is 0, by Eqn. (9b) with the characteristic time constant

$$\tau = VL/AD \quad (19)$$

Eqn. (19) is a special case of the general expression (13) where the first term predominates and $P = D$ because $K = 1$. In other words, moisture diffusion through an opening does not differ conceptually from diffusion through a thin and/or non-absorbing membrane.

The presented model tacitly assumed that the air in the opening is not disturbed. We can expect that with larger openings ambient air motion, e.g., wind may accelerate the process of moisture exchange through some kind of pumping action.

6. Variable ambient humidity

In this chapter we will try to find out how the humidity inside a container or a package c_i responds to variations of the ambient humidity c_a . We will be especially interested in the rate of these changes and how their amplitude compares with that of ambient.

As illustrated in Fig. 4, a change in the ambient air humidity brings about a reluctant change in the inside humidity. We can see also in this figure that

if the variations of c_a are frequent, c_i can barely follow the outside humidity value. Thus the container walls work as an *averaging factor* for the outside conditions.

In order to prove this point and understand better the dependence of the averaging properties of diffusive walls on the frequency of the ambient humidity changes and the ingress rate constant (or time constant) we will assume here that the changes of the ambient absolute humidity have a sinusoidal character, as in Eqn. (20).

$$c_a = c_{oa} + a \sin \omega t \quad (20)$$

where ω is, as usual, the oscillation's angular frequency ($\omega = 2\pi\nu = 2\pi/T$) and a is the oscillation's amplitude. This has been shown in Fig. 6.

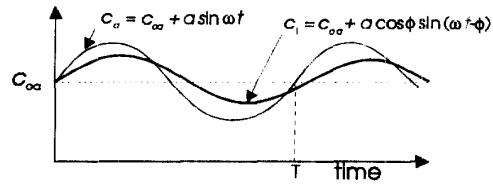


Fig. 6. Ambient humidity oscillations (c_a) and the inside humidity response (c_i)

The electrical analogue of the described situation would be powering of an RC circuit with an alternating voltage. However, unlike voltage, humidity can never be negative and thus there must be a constant factor c_{oa} included in it as in Eqn. (3). Besides, the amplitude can never be bigger than this constant term ($a \leq c_a$)

It is not the intention of the author to imply that real humidity changes are sinusoidal in nature. The assumption's purpose is to make the problem relatively simple and to enable one to follow the role the relationship between frequency of air humidity change and the system's time constant. Besides, any periodical change may be expressed as a Fourier series of sinusoidal oscillations and relations proved in this chapter should be also valid for any real life periodical humidity changes.

In order to model the described situation we have to go back to the original differential equation of moisture diffusion into enclosure, i.e., Eqn. (12) which can be expressed as

$$\frac{dc_i}{dt} = \frac{1}{\tau} (c_a - c_i) = k(c_a - c_i) \quad (21)$$

where the reciprocal of the time constant has been defined as the "rate constant" k of the moisture ingress into the enclosure.

$$k \equiv 1/\tau \quad (22)$$

Substituting the expression (20) for the ambient humidity into Eqn. (21) we have a differential equation

$$\frac{dc_i}{dt} + kc_i = kc_{oa} + ak \sin \omega t \quad (23)$$

Assuming the initial conditions $c_i = c_{oa}$ at $t = 0$, we can integrate this equation to obtain the response of internal humidity to the ambient humidity oscillations:

$$c_i = c_{oa} + a \frac{k\omega}{\omega^2 + k^2} \exp(-kt) + ak \frac{k \sin \omega t - \omega \cos \omega t}{\omega^2 + k^2} \quad (24)$$

This is very similar to the response of an RC circuit to alternating voltage.

Now, if we define an angle ϕ such that

$$\frac{k}{\sqrt{\omega^2 + k^2}} = \cos \phi \quad \text{and} \quad \frac{\omega}{\sqrt{\omega^2 + k^2}} = \sin \phi$$

we can express this dependence as

$$c_i = c_{oa} + a \sin \phi \cos \phi \exp(-kt) + a \cos \phi \sin(\omega t - \phi) \quad (25)$$

Eqn. (25) contains two terms, the exponential one and the trigonometric one. For long times the exponential term vanishes and we have

$$c_i = c_{oa} + a \cos \phi \sin(\omega t - \phi) \quad (t \rightarrow \infty) \quad (26)$$

We can see thus that the internal humidity will undergo oscillations with the same frequency as that of the ambient but phase shifted by an angle

$$\phi = \arccos \frac{k}{\sqrt{\omega^2 + k^2}} = \arccos \frac{1}{\sqrt{1 + \omega^2 \tau^2}} \quad (27)$$

and that the amplitude of oscillations oscillation will be attenuated by the factor of

$$f \equiv \cos \phi = \frac{k}{\sqrt{\omega^2 + k^2}} = \frac{1}{\sqrt{1 + \omega^2 \tau^2}} \quad (28)$$

The internal humidity concentration as a function of time is compared with the ambient humidity in Fig. 6.

When the ambient humidity oscillations are frequent as compared to the ingress rate constant (i.e., $\omega \gg k$ or $\omega t \gg 1$), the attenuation factor $f \rightarrow 0$, inside humidity oscillations are very small and c_i is close to a constant averaged value, in this case c_{oa} . The phase shift approaches then $\pi/2$ (90°). On the other hand, if the humidity changes are relatively infrequent ($k \gg \omega$ or $\omega t \ll 1$), the attenuation factor $f \rightarrow 1$, and the inside humidity follows closely the ambient, both in value and in angle (the phase shift close to zero).

III. EXPERIMENTAL RESULTS

The experiments described in this chapter were performed in order to verify the applicability of the models described in the preceding chapters to moisture ingress time constants. It was also necessary to determine relevant transport properties of the materials used in the model studies.

1. Materials and measuring methods

The wall materials used for containers were: (1) Lexan 9034-112, a clear polycarbonate sheet material from General Electric, (2) ABS, a white, non-transparent acrylonitrile-butadiene-styrene copolymer sheet material from Commercial Plastics. As the window material, silicone rubber (methylvinylsiloxane filled with silica, 40 durometer) from BISCO Products was used. All the containers were solvent welded.

With steady state experiments the amount of water which permeated into the container was measured periodically through the total weight of the container (i.e., container + desiccant) With the non-steady state experiments moisture concentration inside the container was assessed as relative humidity using a CT485 S Humidity Meter equipped with a CT485RV-RP humidity probe, from Omega Engineering, Inc., Stamford, CT, which was calibrated using a series of saturated salt solutions of known equilibrium RH. The experiments were performed at a constant temperature thus relative changes of the measured relative humidity (RH) were directly equivalent to absolute humidity (c_a).

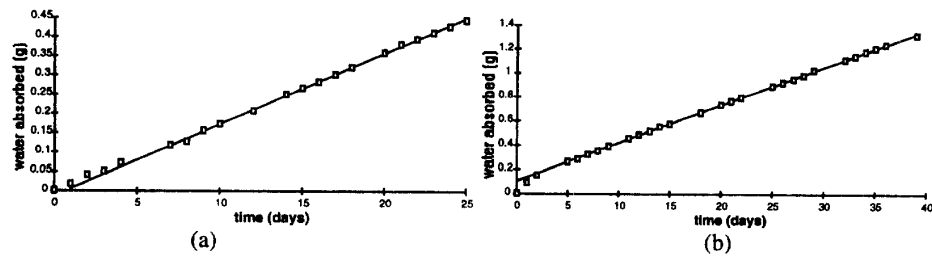


Fig. 7. Moisture ingress into a 8x8x4 cm (a) Lexan (b) ABS box (wall thickness 0.3 cm) with desiccant.

2. Determination of P from steady state experiments

For each plastic material studied, two 8 x 8 x 4 cm boxes were prepared (sheet thickness 0.3 cm), one containing ca. 30 g of drierite and the other with ca. 25 g of silica gel. The boxes were weighed with the 10^{-4} g accuracy and placed in an environmental chamber at 25°C/98% RH. The boxes were withdrawn and weighed daily for a period of 25 days for Lexan and 39 days for ABS. A steady state was established after 5 days for both materials. The P values were determined from Eqn. (5) using a linear regression fit for Q values collected after this time. (Fig. 7) Results for the drierite and silica gel desiccants were identical within the experimental error and the P values (in the same units as D , see Appendix) thus calculated are shown in Table 1.

3. Determination of D and K from sorption studies.

As D values for the plastic materials studied were either not available or unreliable, a series of sorption and desorption experiments were performed. For each sheet material two slabs (8 cm x 4 cm x 0.6 cm) were prepared. The slabs were dried for 3 weeks in a desiccator and placed in a 98% RH/25°C chamber. Their weight was followed periodically for about 150 hrs (1 week) in order to obtain the weight gain M_t and then equilibrated in the same conditions for another 3

weeks in order to obtain the M_{eq} value. For each material weight gains from two slabs were averaged.

Diffusion coefficients were determined from the slope of plots of M_t/M_{eq} vs. square root of time utilizing the validity of Eqn. (29) for the initial sorption period [6]

$$\frac{M_t}{M_{eq}} = \frac{2}{l} \sqrt{\frac{Dt}{\pi}} \quad (29)$$

where l is the half-thickness of the slab, ($l = L/2$). Linearity was maintained to $M_t/M_{eq} = 0.7 - 0.8$ (see Fig. 8). The diffusion coefficients thus calculated are shown in Table 1.

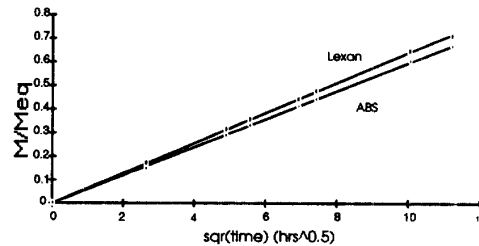


Fig. 8. Sorption into plastic slabs (thickness 0.6 cm). M/M_{eq} as function of square root of time

Table 1. Moisture transport properties of the studied materials

	Polycarbonate	ABS	Silicone rubber
D (cm ² /s)	8.06×10^{-8}	6.99×10^{-8}	n/a
P (cm ² /s)	1.12×10^{-5}	1.92×10^{-5}	2.78×10^{-5}
K	141	274	n/a

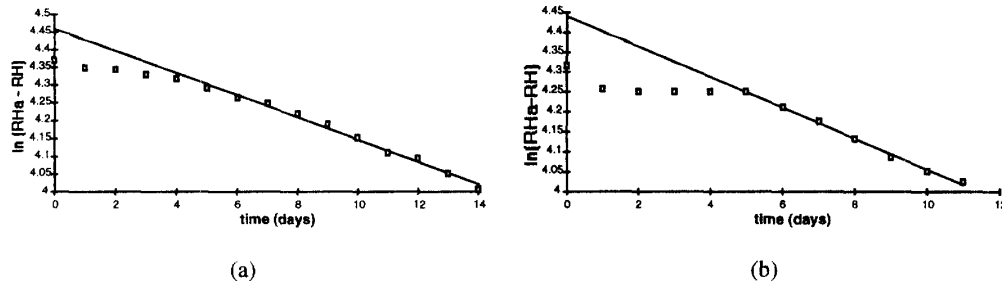


Fig. 9. Moisture diffusion into a 59 cm x 19 cm x 12.5 cm (I.D.) plastic box (wall thickness .6 cm) placed in a 25°C/98% RH chamber. Least square fit was applied for times > 5 days. (a) polycarbonate (b) ABS

Desorption was studied analogously in a desiccator and similar D values were obtained. For polycarbonate the desorption D is somewhat lower than the sorption D which would suggest that D increases with water concentration [6a] and for ABS D is somewhat higher for desorption than for sorption and thus D seems to decrease with water concentration. [6a].

From the P and D values determined in the described experiments the sorption equilibrium constant K can be calculated as $K = P/D$ and the results (as non dimensional numbers, see Appendix) are shown in Table 1.

4. Testing QSS: diffusion through thick walls

In these transient experiments diffusion of moisture into plastic containers with no desiccant was studied. The container dimensions were 59 cm x 19 cm x 12.5 cm (I.D.) and the wall thickness was 0.6 cm. The RH probe and a magnetic stirring bar were sealed (solvent welded) inside the container and the container was placed on a magnetic stirrer in an environmental chamber at 25°C/98% RH and the values of RH, starting with RH_0 were followed.

Plots of $\ln(RH_a - RH)$ vs. time for both materials are shown in Fig. 9. This type of plot should be linear if the Eqn. (11) is valid. In our experiment, the plot becomes fully linear after 5 days into the experiment. Least square fits of data collected after that time result in the experimental values for the time constant $\tau = 32$ days for the polycarbonate box and $\tau = 26$ days for the ABS box. Utilization of the QSS model, Eqn. (13) in which $\tau = VL/AP + L^2/2D$ and the water transport data of Table 1 to estimate the time constant results in the τ values of 28 days and 30 days, respectively. We see that numerically the QSS model predicts very well the experimental time constants, although the single exponential Eqn. (11) does not represent very well the humidity - time profile, especially in the beginning. With both materials the second term predominates and thus we can expect that the transient "diffusion into a slab" model should approximate this profile better. Thus, the experimental RH as a function of time is shown in Fig. 8 together with the ones calculated from first 8 terms of the appropriate modification of Eqn. (17), viz.,

$$RH = RH_0 + (RH_a - RH_0) \left[1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right) \right] \quad (30)$$

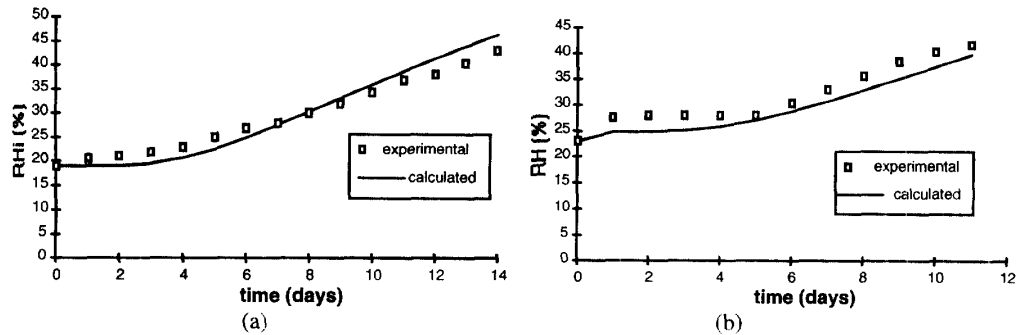


Fig. 10. Experimental and predicted RH values inside plastic containers. The predicted RH's were calculated from Eqn. (19) using first 8 terms of the expansion and D from Table 1. (a) polycarbonate, (b) ABS

As we can see in Fig. 10, the agreement is, indeed, very good.

5. Testing QSS: diffusion through silicone rubber window.

In this experiment in the previously used polycarbonate container a 7 cm x 7 cm square opening was cut out and was covered with 1/16 inch silicone rubber pad which was fastened by a screwed-in frame thus forming a "rubber window". This is a thin non-absorbing membrane where the first term of Eqn. (13) should predominate and this arrangement is similar to having a rubber gasket.

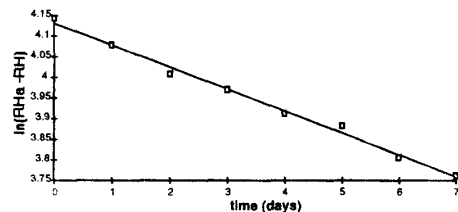


Fig. 11. Moisture ingress into the polycarbonate container (see Fig. 7) equipped with a 7 cm x 7 cm silicone rubber window of thickness 1/16 inch.

The experiment was performed as above and the plot of $\ln(RH_a - RH)$ is shown in Fig. 11. The plot is clearly linear and the time constant derived from the slope is 18.8 days. Since for this thin window $\tau = VL/AP$, the rubber permeability P could be calculated and is given in Table 1. [For a more accurate treatment the concurrent moisture

ingress through the ABS walls should also be considered. However, since the wall material was saturated to an uncertain degree with water in the previously described experiment and the diffusion through walls is slower than through the silicone window, this effect was not taken into account here.]

Thus with the small amount of nonabsorbing membrane the QSS model fits perfectly the experiment.

6. Diffusion through openings

In both described experiments holes were bored in a described above Lexan container their total cross section area being 0.125 cm². The containers were placed in a 25°C/98% RH environmental chamber and the moisture concentration inside the container was followed as before. The presence of an efficient fan inside the environmental chamber rendered the experiment conditions equivalent to those during a strong wind.

(a) Sixteen 0.1 cm holes

The results of the moisture ingress into an ABS box with 16 0.1 cm holes (total area 0.125 cm²) are shown in Fig. 12.

From the slope of the mostly linear plot of $\ln(RH_a - RH)$ vs. time a time constant of 148 hrs (6 days) was obtained. This is longer but of the same order of magnitude as the value of 3.25 days calculated from Eqn. (20) using the literature value of water diffusion coefficient (0.24 cm²/s) [15]. Thus the observed ingress rate was somewhat slower than expected. One way of explaining this

small deviation is the desiccating action by Lexan after it diffused into the enclosure. It was shown above that Lexan can absorb significant amounts of water. Besides, the accuracy of the hole diameters is somewhat uncertain. Thus the experiment with 16 0.1 cm holes showed a general agreement with the QSS exponential kinetics of moisture ingress Eqn. (9), with the time constant approximating the one calculated from the QSS model.

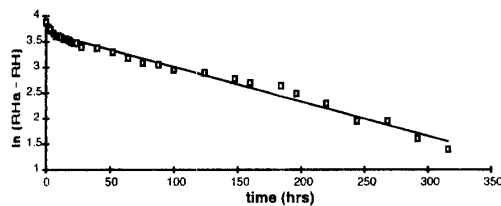


Fig. 12. Moisture ingress into a ABS box with sixteen holes of 0.1 cm diameter

(b) One 0.4 cm diameter hole.

The moisture ingress through one hole of 0.4 cm diameter into the Lexan container is shown in Fig. 13. The plot of $\ln(RH_a - RH)$ vs. time is not very linear, and what is even more important, the time constant derived from the slope is 15.6 hrs (0.65 days), approximately an order of magnitude shorter than with 16 0.1 cm holes. This is attributed to the fact that in the environmental chamber pulsating pressure changes are observed due to the fan action equivalent to a wind in a real life situation and with a rather large hole this translates into an additional mechanism of air and moisture exchange.

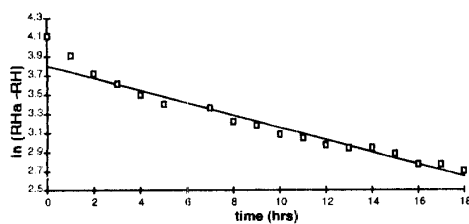


Fig. 13. Moisture ingress into an ABS box with one hole of 0.4 cm diameter.

Thus the effect of linear hole dimensions (as opposed to the cross-section area) on the rate of moisture ingress due to ambient air motion has been demonstrated

IV. CONCLUSIONS

The process of diffusion into containers can be described by the quasi - steady state model where moisture in the container is given by Eqn. (9) or the more general Eqn. (11) with the time constant given by Eqn. (13).

For thin and/or small and/or non - absorbing walls the first term of the Eqn (13) predominates and the time constant depends on the material's permeability coefficient P . It is also a function of the container's geometry (V and A). In this situation a single exponential time - humidity profile is observed experimentally.

For thick and/or absorbing walls (or a small internal cavity volume) the second term of Eqn. (13) predominates. The diffusion constant D is the deciding transport property and the moisture diffusion kinetics does not depend on the container's geometry, only on the wall thickness. With thick and/or absorbing walls replacing some (or even most) walls with metal or ceramic may not reduce the moisture diffusion rate into the enclosure significantly. Experimental moisture ingress rate into containers with thick/absorbing walls is well predicted by the time constant calculated from Eqn. (13) but the detailed humidity time profile is better predicted by the multiexponential Eqn. (17) derived from the transient model.

Diffusion through the air layer in the openings follows the quasi - steady state model for non-absorbing membrane characterized by the exponential character of moisture exchange and in which the characteristic time constant is calculated as $\tau = VL/KD$, i.e. assuming that $P = D$. With larger openings winds and other ambient air movements can significantly speed up the rate of the process. One can assume that in this situation above a certain linear dimension of the opening the system may be considered to be totally open.

In order to determine the attenuation of ambient humidity changes by the enclosure it is important to compare the angular frequency ω which is characteristic of a given geographic area to the diffusion rate constant k (i.e. $1/\tau$) which is characteristic of a given enclosure. For the enclosure, in order to shield the equipment from

the ingress of humidity, the ingress rate constant k should be much smaller than the frequency of ambient humidity changes to ensure stable conditions in the enclosure. This is valid irrespective of the ingress route and mechanism.

The ambient relative humidity changes constantly during the day as the temperature changes. On the other hand changes of the absolute humidity of air are rare [16,17]. Only the exchange of the whole air mass in the region can result in a perceptible change in absolute humidity (which is usually referred to in weather reports as dew point). The frequency of such exchanges is characteristic of the given geographic area. For instance, in Eastern Ontario there would be a new air mass coming weekly to monthly but in Florida the same air mass may hang around for about six months.

Let us consider the 59 cm x 19 cm x 12.5 cm ABS container (wall thickness was 0.6 cm) used in the described above experiments. Its characteristic time constant is 28 days. In eastern Ontario where the absolute humidity can change monthly ($\nu = 1/30 \text{ days}^{-1}$, $\omega = 0.89 \text{ days}^{-1}$) the expected attenuation factor is 0.16. The ambient humidity effects can thus be strongly attenuated by this container. In Florida, however, with 6 month long air mass exchange cycles ($\nu = 1/182 \text{ days}^{-1}$, $\omega = 0.035 \text{ days}^{-1}$) the attenuation factor will be 0.8. In other words, the humidity variations inside the container will amount to 80% of the ambient humidity changes. Since the effective time constant of the box will be even shorter due to the container's imperfections, cabling etc., the benefit of having the enclosure is minimal in this climate. After 6 month in humid air a cold front may cause condensation of water inside and result in equipment failure.

It is worth stressing that the above considerations are not limited to outdoor equipment. Except with the buildings which are actively humidity controlled by drying and/or humidifying, the indoor air has the same absolute humidity as the outdoor air and follows the same humidity changes, even if the building is air conditioned. The temperature related relative humidity difference between the outdoor and indoor air does not influence the moisture ingress rate (the temperature difference will influence diffusion coefficients and permeabilities, however). On the other hand, the relative stability of the indoor air temperature should render condensation and failure less likely.

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VI. APPENDIX. The Problem of Dimensions of Permeability and Diffusion Coefficients

The diffusion coefficient D has dimensions of length² time⁻¹ and is usually expressed as m² s⁻¹ or cm² s⁻¹. However, one encounters a mind boggling variety of units for the permeability coefficient P [8-10,14]. Although P is defined as KD , for most units P is functionally defined from Eqn. (4) or similar such that, e.g.,

$$[P] = (\text{amount of gas}) (\text{film thickness}) / (\text{film area})(\text{partial pressure gradient})$$

Those who work with gasses often express the amount of gas in cm³(Standard Temperature and Pressure) and pressure in mm or cm Hg. Thus a typical and a most frequently encountered unit for P is

$$(\text{cm}^3 \text{ at STP})(\text{cm})/(\text{cm}^2)(\text{s})(\text{cm Hg})$$

This means that the unit of solubility constant K is defined here as

$$[K] = (\text{cm}^3 \text{ at STP})/(\text{cm}^3)(\text{cm Hg})$$

Yasuda proposed [14] that *units of permeability be identical to those of diffusion coefficients, e.g., cm² s⁻¹ which is equivalent to having a dimensionless solubility constant K* . In this system concentration units of water in the vapour phase and in the membrane are the same (e.g. g/cm³, mole/l, etc.) but it does not matter which ones. Simple considerations of gas laws lead [14] to the following relationship which can be used when comparing the literature data for P with those determined in this paper

$$P [\text{in cm}^2 \text{ s}^{-1}] = 76 \cdot (T/273) \cdot P [\text{in (cm}^3 \text{ at STP})(\text{cm})/(\text{cm}^2)(\text{s})(\text{cm Hg})]$$

where T is the absolute temperature. For diffusion at 273 K (0°C) the conversion factor is simply 76 and for 298 K (25°C) it is 83. Some conversion factors between other units encountered in literature are given in ref. [10]

The convention proposed by Yasuda allows one an easy comparison of P and D values which is especially important when we want to compare diffusion through the wall material and an opening in the wall.

VII. ACKNOWLEDGMENT

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