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MEASUREMENT OF WATER VAPOR TRANSMISSION THROUGH INSULATING GLASS SEALANTS

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ABSTRACT

The use of a sensitive electrobalance in the determination of the barrier characteristics of the materials of construction for insulating glass windows is described. The principles underlying the performance of insulating glass units for energy conservation are discussed. The mathematics of the transport process through these barriers are also developed.

INTRODUCTION

The emphasis on energy conservation has focused increased interest on insulating glass window units for building construction. These are made by separating two or three glass panes with hollow metal spacers which contain a sorbant for water and organic vapors. The structure is bound together by an organic mastic which functions as both a structural component and as a barrier to slow the passage of water vapor to prevent condensation on the interior surfaces. Obviously, when this occurs light transmission is affected and the window must ultimately be replaced at considerable expense.

In addition to producing increased dew points water vapor in sufficiently high concentration may actually displace the organic binder at the glass interface causing loss of adhesion and subsequent structural weakness[1-3].

Another deleterious effect of water vapor is produced as the ultraviolet light from the sun concentrates at the interface due to multiple reflections from the glass surfaces. The radiant energy absorbed by the organic binder and barriers tends to cause free radicals to form because of polymer cission.

In the presence of water molecules they are terminated, thus generating low-molecular-weight compounds instead of recombining in some different but high molecular configuration. The former may have a reasonably high vapor pressure at summer time temperatures within the window which can be as high as 75°C. At night fall the drop in temperature causes the vaporized organic material to deposit on the interior glass surfaces to produce an undesirable fog.

However, as long as there is sufficient active sorbant within the spacers both the aqueous and organic vapors are sequestered and prevented from causing harm. Ultimately, of course, the former becomes saturated and the unit has to be replaced. Obviously, then the life span of the window is determined by the barrier efficiency of the sealant or binder and the sorptive capacity of the materials within the spacer.

It is, therefore, important to obtain information on the moisture vapor transmission of the sealant system, its fogging potential and the sorptive capacity of the desiccant in the spacer in order to project the performance and longevity of an insulating glass window.

In this paper, only the MVT aspect will be discussed. It is not its purpose, however, to describe all the methods which have been used to determine the MVT characteristics of films. However, two methods in common use are the Honeywell tester[4] and the Payne Cup; so they deserve special discussion.

In the former case, a mechanically perfect membrane of approximately 122 cm^2 in area is mounted between 2 half cells. After insuring a perfect seal between the membrane and the cells, water vapor at some definite pressure and temperature is admitted at one side and allowed to permeate through the film until a change of 1% in relative humidity is attained (from 10–11%) which is measured by an electronic hydrometer. The time required to reach this condition is used to calculate the MVT usually expressed as[5]: Grams/100 $in.^2$/24 Hours.

The Payne cup[6] is simply a metal container for a desiccant such as calcium chloride. Across its top is mounted the film whose permeability is being measured. Here again, it is obvious that care must be exercised to insure that a membrane is obtained which is leak proof. The rate of weight gain of the unit after exposure to conditions of interest is used to calculate the MVT.

Certain difficulties in these two methods are immediately obvious from what has been described above. In both instances, care must be taken to prepare a mechanically perfect film. It is then mounted in the cell in such a manner as to insure that all transmission takes place only across the film and not by leakage through spurious routes. Experience indicates that this is no easy task, particularly with films which tend to be somewhat brittle or which may become so under the conditions of measurement. In the case of the Payne cup, an additional disadvantage is the weight of the metal container which may exceed the sensitivity range of the balance used to determine the weight gain, particularly for those cases where the film barrier properties are exceptionally good and very little moisture permeates through the membrane.

Another disadvantage of methods using an unsupported membrane as a barrier is the impossibility of determining how the MVT as well as other functional characteristics change after exposure of the barrier in service. It is usually not possible to obtain a sample in the proper condition under these circumstances.

One purpose of this paper is to describe a gravimetric method for the determination of the barrier properties of an insulating glass sealant (particularly its MVT) which eliminates some of the disadvantages described above. Application to the determination of fogging characteristics of sealants as well as the adsorptive capacities of desiccants and absorbants such as molecular sieves under varying conditions will be discussed in a later presentation.

The method employs an electrobalance, sensitive to 10^{-8} g which is used to measure weight changes under controlled experimental conditions. These data are used to calculate a diffusion and a solubility coefficient. Their product is equal to the permeability coefficient[7]. This is the important parameter that uniquely defines the barrier properties of the film since it is unvarying at constant temperature regardless of the pressure differential (assuming concentration independence) cross sectional area, thickness and exposure time.

Equation (1) is the mathematical expression

$$Q = \frac{PA\,(\Delta\,p)\,t}{l} \tag{1}$$

Where Q is the weight of volume of gas transmitted at standard temperature and pressure, A is the film area, $\Delta\,p$ is the pressure difference between one side of the membrane and the other, t is the time during which the amount Q is transmitted and l is the film thickness. P here is the permeability coefficient which for most films is unvarying at constant temperature regardless of the value of the other factors in eqn (1). Substitution of the value of P in eqn (1) permits the calculation of MVT regardless of how it is defined. For those interested in the theoretical background of the method described in more detail below, an appendix is included.

EXPERIMENTAL

The main features of the moisture vapor transmission apparatus consist of a Cahn Electrobalance model RG-HV and high vacuum glass enclosure, Houston Instrument series 5000 recorder model number 5113-5, Welch Duo-Seal vacuum pump model number 1400 and a constant temperature box controlled by a West 802M series temperature controller. The apparatus is shown schematically in Fig. 1 and photographically in 1B and 1C.

The Cahn Electrobalance system is not only economical but also provides capability for analyses of field aged samples since only minute specimens are needed.

The density of the sealant must be known to make the required gas or vapor solubility calculations which are expressed as cubic centimeters of gas at standard temperature and pressure per cubic centimeter of sample*. This is easily determined by die cutting a section of the sealant and measuring its thickness. Multiplication of the area and thickness gives the volume. The weight of the sample is obtained at the start of the determination from which the density is calculated according to the

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* While the solubility coefficient is generally expressed as cubic centimeters of vapor at 273° Celsius and 76 centimeters pressure per cubic centimeters of polymer, it is expressed in the calculation as grams of water vapor per cubic centimeters of polymer since the quantity transmitted is recorded as a weight.

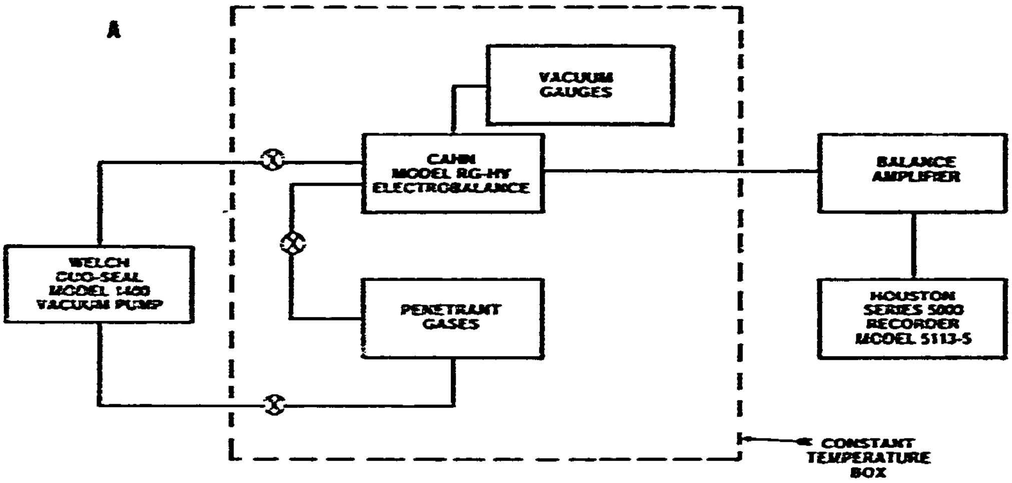

Fig. 1. (A) Schematic of Cahn balance system, (B) Photograph Cahn balance set-up enclosed in temperature control box. (C) Cahn balance set-up with recorders.

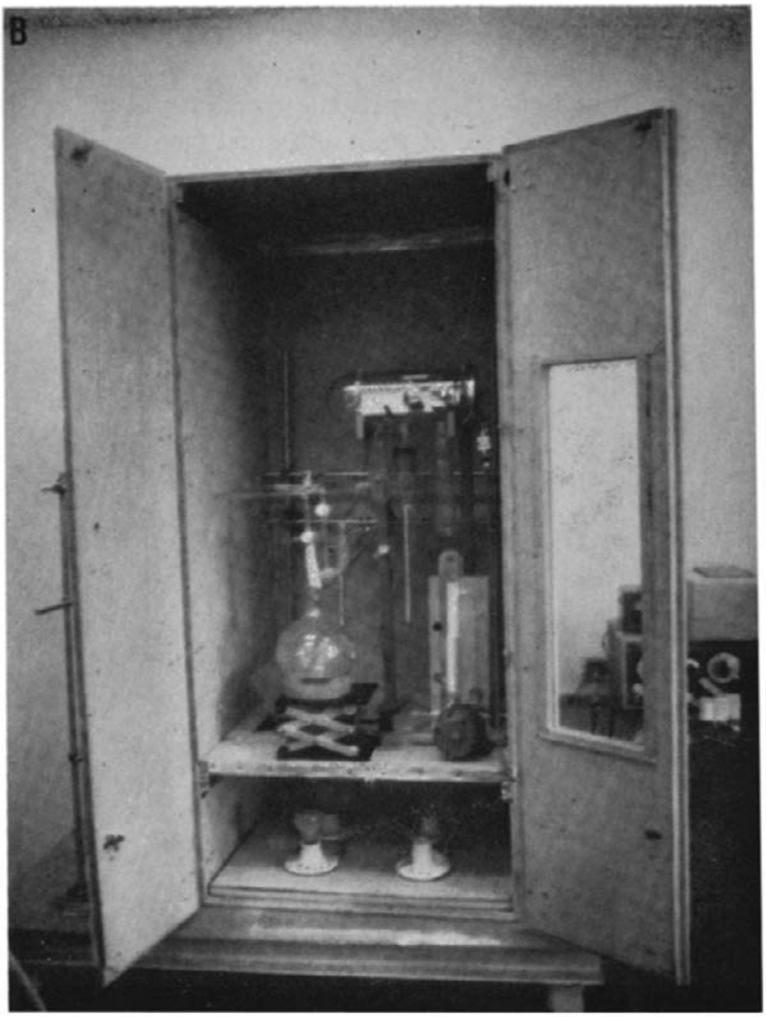

Fig. 1 (B)

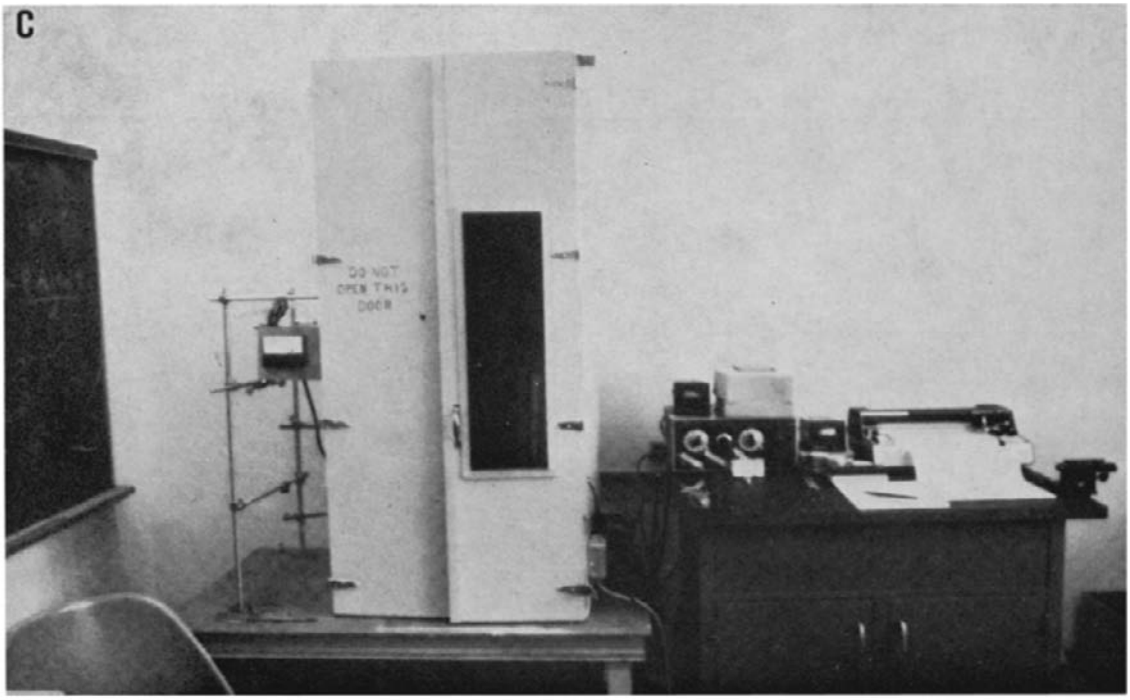

Fig. 1 (C)

M/V formula. Whether the samples have been obtained from a previously aged window and are of irregular shape or from uniformly cast films, they can be cut to proper size and shape. In the work described here, an American Optical microtome model number 900 was used. Due to the nature of the Cahn Electrobalance and experimental time considerations the samples are prepared so that they weigh between 30–80 mg and thickness ranges between 0.250–1.75 millimeters (10–70 mils).

After preparation, the sample is mounted on the balance and degassed at 100°F and $\approx 1 \times 10^{-4}$ torr until a constant weight is indicated on the recorder. After the sample is equilibrated in this manner (about 2 hours) the system is isolated. The next step is to admit water vapor to the desired pressure usually equivalent to 75% to 90% R.H. and record the weight pickup per unit of time. Eventually, there is no further weight increase and the difference between the final and original values is the amount of water vapor in the sample. This number divided by the volume of the sample provides the weight of moisture per cubic centimeter of sample at the water vapor pressure of the experiment. Division by this pressure yields the solubility per centimeter of mercury pressure or the solubility coefficient* at the temperature of the experiment.

To obtain D, the diffusion coefficient, the time (t) at which 1/2 the equilibrium amount of water vapor in the sample is taken from the plot of Q vs. t (Fig. 2) and substituted in the equation:

$$D = 0.04919/t_{1/2}/l^2)\ \text{cm}^2\ \text{min}^{-1} \qquad (2)$$

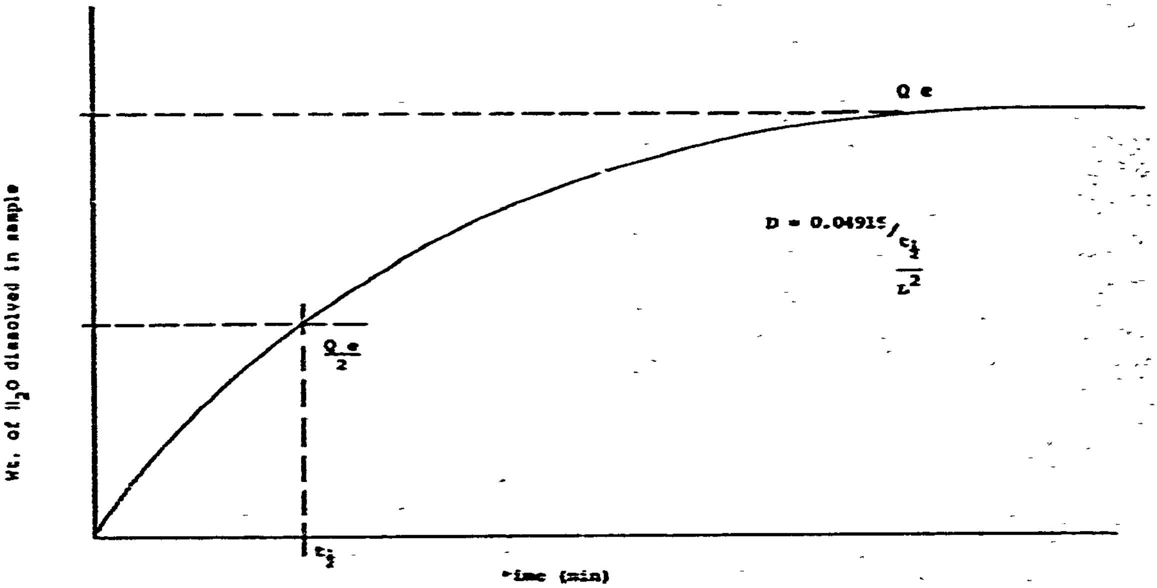

Fig. 2. Water vapor sorption curve as a function of time.

where l is the sealant sample thickness. Since D and S are now known, P is determined by multiplication:

$$P = D \times S \,\text{cm}^2\,\text{mm}^{-1} \times \text{g/cm}^{-3} = \text{g min}^{-1}\,\text{cm}^{-1} \qquad (3)$$

Figure 2 represents a plot of water vapor pickup versus time.

EXPERIMENTAL DATA

The following are examples of the data produced in these measurements:
Commercial polysulfide sealant
Density 1.8 g cm^{-3}
Volume 3.15×10^{-2} cm^3
Temperature = 100°F or 37.8°C.
H_2O vapor pressure 3.8 cm Hg at 100°F ≡ 78% RH
Sample thickness 5.21×10^{-2} cm (20.5 mils)
Sample weight 5.66×10^{-2} g
Weight gain at equilibrium (Qc) 2.89×10^{-4} g or 9.2×10^{-3} g cm^{-3} of sample
When $Q/Qe = 1/2$, $t = 4.4$ min from eqn (2)

$$D = 3.2 \times 10^{-5}\ \text{cm}^2\,\text{min}^{-1}$$

Solubility coefficient: $(S) = 2.42 \times 10^{-3}$ g cm^{-3} per cm Hg
From $Qe = S \times$ pressure (cm Hg) (4)
Permeability coefficient:

$$P = D \times S = 7.31 \times 10^{-8} = \text{g cm}^{-1}\ \text{cm Hg min}^{-1}.$$

An example of how the permeability coefficient may be used to calculate the transmission rate expressed as the number of grams of water Q transported per 24 hours per 100 square inches is given below:

Polysulfide permeability coefficient (P) = 7.31×10^{-8} g cm^{-1} cm Hg min^{-1}.

Cross section area (A) = 100 in.^2 = 645.2 cm^2 (t) = 24 h = 1440 min

Vapor pressure difference (ΔP) from 10 to 100% at 100°F per Honeywell conditions = 4.5 cm

Thickness (l) = 5.1×10^{-2} cm (20 mil film per Honeywell conditions)

Substituting in eqn (1)

$$Q = P\,A\,\Delta p\,t/l \quad (1)$$

$$Q = \frac{7.3 \times 10^{-8} \times 645.2 \times 1440 \times 4.5}{5.1 \times 10^{-2}} = 5.77\ \text{g}/100\ \text{in.}^2/24\ \text{h}/5 \times 10^{-1}\ \text{mm}$$

Comparable Honeywell data yield a permeability coefficient of 7.23×10^{-8} and a transmission of 5.77 g/24 h 100 in.^2 (645.2 sq. cm)

A sample of polyisobutylene tape used as a primary barrier in the insulating glass system was also run on the electrobalance. This would not be practical in equipment requiring a perfect membrane sample because the softness and flowability of the material would not permit a useful film to be made which would withstand the pressure.

As indicated in Table 1 the polyisobutylene is a very efficient water vapor barrier being about 300 times better than the polysulfide. This is the basis for an important advantage of dual seal system in insulating glass units as explained below.

The amount of water vapor transmitted is proportional to the difference between the high vapor pressure on the exterior side and the lower one on the interior side (other things being equal) of the secondary seal, i.e., the polysulfide. This lower pressure now becomes the high pressure side of the primary or polyisobutylene seal. The pressure difference on either side of the secondary seal is now substantially less than for the primary which of course enhances its barrier capabilities. Thus, two

TABLE 1

PERMEABILITY DATA

	Honeywell	*Cahn*
Polysulfide		
Permeability coefficient	7.23×10^{-8}	7.31×10^{-8}
Trans rate G/24 h	5.71	5.77
Polyisobutylene		
Permeability coefficient	3.3×10^{-10}	2.54×10^{-1}
Trans rate G/24 h	0.026	0.020

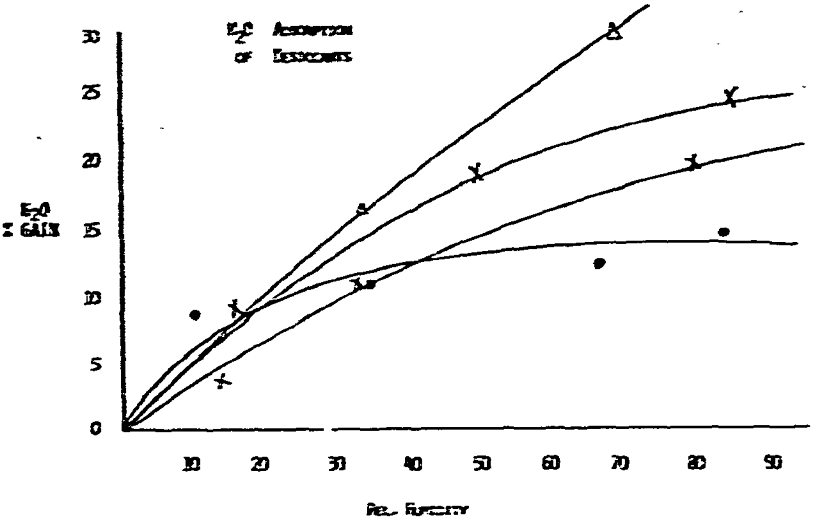

Fig. 3. Range of water sorption for some typical commercial desiccants measured at 100°F. Δ = Silica Gel; × = SiO_2 Gel ÷ Mol Sieve; ● = Mol Sieve.

benefits accrue by the use of the dual system; one because the polyisobutylene is about 300 times a better barrier by itself than the polysulfide and the second because the lower pressure differential across it favors the diminished passage of water into the interior of the unit according to eqn (1).

Since the electrobalance is an extremely sensitive weighing instrument, it has been used to determine the sorption characteristics of different dessicants. Figure 3 indicates the range of water sorption for some typical commercial types measured at 100°F. In future work, more detailed studies of sorbants will be made. The Cahn apparatus will also be used to quantify fogging characteristics of different sealants as well as their components.

CONCLUSION

The advantages of the use of the electrobalance gravimetric method are:

1. Small sample needed (about 50 mg).
2. Sample need not be continuous as required in other methods in which a perfect or hole-free film must be used.
3. Difficult leak-free permeability cell sealing is eliminated.
4. May be employed to [illegible] barrier property changes which have occurred in field-exposed units.
5. Can determine sorption characteristics of desiccant for water vapor and other volatile materials.
6. Can provide quantitative fog data.
7. May be used to study sealant and glazing compatibilities.

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APPENDIX

The basic equation for the gravimetric method described above is

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{5}$$

dc/dt = rate of concentration change of permeant within film, D is diffusion coefficient and x is distance within the film at any concentration.

Equation (5) is one of the mathematical relationships deduced by Fick who was concerned with transmission phenomena of matter and energy. The solution of the differential eqn (5) depends on the type of experiment to be run. In the method described here, a sample of known thickness (l) is suspended from the balance and exposed to vapor at some predetermined pressure. Under these conditions, the initial concentration of vapor within the film is zero and the value outside it being the starting concentration (or pressure). At equilibrium, there is no concentration gradient within the film and the solution to eqn (5) is:

$$\frac{Qt}{Qe} = 1 - \frac{8}{\pi^2}\sum_{M=o}^{M=x}\frac{1}{(2M+1)^2}\left\{\text{exp.}\frac{-D(2M+1)^2}{l^2}\pi^2 t\right\} \tag{6}$$

Qt = weight gain of film at time (t)
Qe = equilibrium weight gain of film
where m = 0, 1, 2 etc
D = diffusion coefficient
l = film thickness

Following eqn (6), the value of t/l^2 for which $Qt/Qe = 1/2$ is written

$$(T/l^2)_{1/2} = -\frac{l_2}{\pi^2 D}\left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right] \tag{7}$$

within an error of 0.001 % eqn (7) may be simplified to:

$$D = \frac{0.04919}{(t/l^2)_{1/2}} \tag{8}$$

All of the above make the assumption that D is a constant[9].

The value of the weight gain, when no further change occurs, is Qe which is the solubility of the gas or vapor (in this case H_2O) in the sealant. Since we are dealing basically with barrier materials, the amount of vapor dissolved within the film is usually quite small and is proportional to the vapor pressure. Therefore, the following relationship holds:

$$Q = SP \tag{9}$$

Where S, the proportionality factor, is known as Henry's law solubility coefficient.

At equilibrium there is no further weight gain and no change in concentration of water vapor within the film. Therefore, $dc/dt = 0$.

Substituting in eqn (5)

$$0 = \frac{D\,d^2c}{d\,x^2} \tag{10}$$

Integration of (10) yields

$$P = D\frac{dc}{dx} \tag{11}$$

where P is the integration constant.

Then

$$P\int_0^l dx = D\int_{c_2}^{c_1} dc \tag{12}$$

$$Pl = D(c_2 - c_1) \tag{13}$$

Since $C = SP$ (Henry's Law) (9)

$$P = D(SP_2 - SP_1)/l \tag{14}$$

$$P = DS(\Delta P)/l \tag{15}$$

At unit pressure difference and unit thickness

$$P = DS \tag{16}$$

The total amount of matter that has permeated during time t through a film of area A is then

$$Q = DS(\Delta P)/l \times t \times A \tag{17}$$

$$Q = P(\Delta P)/l \times t \times A \tag{18}$$

Since $P = DS$

Equation (18) is the well-known relationship used in evaluating and quantifying the permeability characteristics of a barrier film.

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