

BARRIER PROPERTIES



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Introduction

- The barrier properties of plastics indicate their **resistance to sorption and diffusion of substances** such as gases and flavor and aroma compounds.
- The **solution and transport behavior of low MW substances in plastics has become increasingly important** in recent years with the widespread and expanding use of polymer films and rigid plastics for food packaging.
- The **selection or development of plastics for food packaging applications** with stringent design specifications relating to their solution and diffusion behavior requires knowledge and appreciation of the many factors which affect those phenomena.

➤ The protection of foods from gas and vapor exchange with the environment depends on the **integrity of packages** and on the **permeability of the packaging** materials themselves.

➤ There are **two processes** by which gases and vapors may pass through polymeric materials:

1. A pore effect, in which the gases and vapors flow through microscopic pores, pinholes and cracks in the materials.

2. A solubility-diffusion effect, in which the gases and vapors dissolve in the polymer at one surface, diffuse through the polymer by virtue of a concentration gradient and evaporate at the other surface of the polymer. This process (**activated diffusion**) is described as **true permeability**.

THEORY

In 1866, **Graham** first postulated that the **permeation process** entailed solution of the gas in the upstream surface of the membrane, diffusion through, followed by evaporation from the downstream membrane surface. **This is the basis for the so called solution-diffusion model.**

The subject was placed on a quantitative basis in 1879 by the Polish physicist **Szygmunt von Wróblewski**, who showed that the **solubility of gases** in rubber obeyed **Henry's law** (at a given temperature, the amount of gas dissolved in a solution is directly proportional to the pressure of the gas) and combined this with **Fick's law** to obtain permeation rate.

Under **steady-state conditions**, a gas or vapor will diffuse through a polymer at a constant rate if a constant pressure difference is maintained across the polymer. The **diffusive flux, J** , of a permeant in a polymer can be defined as the amount passing through a plane (surface) of unit area normal to the direction of flow during unit time as follows:

$$J = Q/At$$

where Q is the total amount of permeant which has passed through area A during time t .

The relationship between the **rate of permeation** and the **concentration gradient** is one of direct proportionality and is embodied in **Fick's first law**:

$$J = -D(\delta c / \delta x)$$

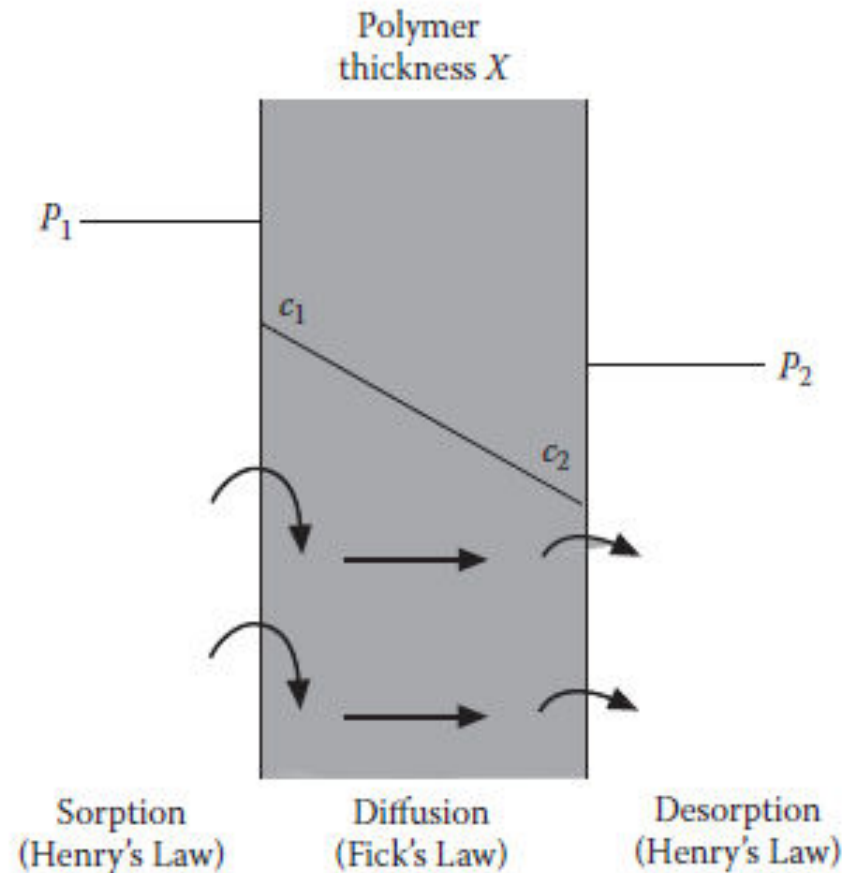
J is the flux (or rate of transport) per unit area of permeant through the polymer,

c is the concentration of the permeant,

D is defined as the diffusion coefficient ,

$\delta c / \delta x$ is the concentration gradient of the permeant across a thickness δx

D reflects the speed at which the permeant diffuses through the polymer; it is a function of temperature and may be a function of concentration.



Consider a polymer X mm thick, of area A , exposed to a permeant at pressure p_1 on one side and at a lower pressure p_2 on the other as shown in Figure. The concentration of permeant in the first layer of the polymer is c_1 and in the last layer c_2 .

If x and $(x + \delta x)$ represent two planes through the polymer at distances x and $(x + \delta x)$ from the high-pressure surface, and if the rate of permeation at x is J mL sec⁻¹, and at $(x + \delta x)$ is $J + (\delta J/\delta x)\delta x$, then the amount retained per unit volume of the polymer is $(\delta J/\delta x)$. This is equal to the rate of change of concentration with time:

$$\frac{\delta}{\delta x}(J) = -\frac{\delta c}{\delta t}$$

A negative sign is used because the concentration of permeant decreases across the material. Under **steady-state conditions**, $\delta c/\delta t = 0$ and $J = \text{constant}$. **When the concentration gradient is zero (i.e., $c_1 = c_2$) there will be no permeation.**

$$\frac{\delta}{\delta x}(J) = \frac{\delta}{\delta x} \left[-D \frac{\delta c}{\delta x} \right] = -\frac{\delta c}{\delta t}$$

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left[D \frac{\delta c}{\delta x} \right]$$

$$\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2}$$

- This is a simplified form of **Fick's second law of diffusion** and applies under circumstances where (i) diffusion is limited to the x-direction and (ii) D is independent of concentration which is usually true in polymers.
- It describes the **unsteady or transient state** for one dimensional diffusion.

STEADY-STATE DIFFUSION

When a steady-state of diffusion has been reached, $J = \text{constant}$ and Equation can be integrated across the total thickness of the polymer X and between the two concentrations, assuming D to be constant and independent of c -

$$JX = -D(c_2 - c_1)$$

$$J = \frac{D(c_2 - c_1)}{X}$$

This expression can be rewritten by substituting for J . This enables calculation of Q , the quantity of permeant diffusing through a polymer of area A in time t :

$$Q = \frac{D(c_2 - c_1)At}{X}$$

When the **permeant is a gas**, it is more convenient to measure the vapor pressure p which is at equilibrium with the polymer, rather than measure the actual concentration. At sufficiently low concentrations, Henry's law applies and c can be expressed as

$$c = Sp$$

where **S is the solubility coefficient** of the permeant in the polymer. S reflects the amount of permeant in the polymer.

$$Q = \frac{DS(p_1 - p_2)At}{X}$$

The product DS is referred to as the **permeability coefficient** or constant and is represented by the symbol P:

$$P = DS$$

Permeability coefficient

Thus, the permeability coefficient is the product of a **kinetic term (D)** which reflects the **dynamics of the penetrant-polymer system** and of a **thermodynamic term (S)** which depends on the **penetrant-polymer interactions**. **P** represents the ease with which a gas permeates through a polymer when subjected to a pressure gradient.

$$P = \frac{QX}{At(p_1 - p_2)}$$

$$\frac{Q}{t} = \frac{P}{X} A(\Delta p)$$

The term P/X is called the **permeance** and is represented by the symbol R . **Permeance is not a property of the material but a performance evaluation indicator.**

There are **four assumptions** made in the earlier simple treatment of permeation.

- First, diffusion is at steady-state.
- Second, the concentration-distance relationship through the polymer is linear.
- Third, diffusion takes place in one direction only (i.e., through the film with no net diffusion along or across it).
- Fourth, both D and S are independent of the concentration.

Deviations

- Although steady-state is usually attained in a few hours for small molecules such as O₂, **larger molecules in barrier polymers (especially glassy polymers) can take a long time to reach steady-state**, this time possibly exceeding the anticipated shelf life.
- Although D and S are independent of concentration for many gases such as O₂, N₂ and, to a certain extent, CO₂, this is **not the case where considerable interaction between polymer and permeant** takes place (e.g., water and hydrophilic films or many solvent vapors diffusing through polymer films).
- Although the **chemical structure of a polymer** can be considered to be the predominant factor which controls the magnitude of P, it also varies with the morphology of the polymer and depends on many physical factors such as **density, crystallinity and orientation**.

UNSTEADY-STATE PERMEATION

- Because of the finite diffusion rate of the solute in the polymer, there is an interval before the steady-state is achieved.
- The situation which exists during this transient or unsteady-state period, where concentration varies with time, is described by Fick's second law, which is a derivative of the first law.

$$Q = \frac{Dc_1}{X} \left[t - \frac{X^2}{6D} \right]$$
$$= \frac{Dc_1 t}{X} - \frac{c_1 X}{6}$$

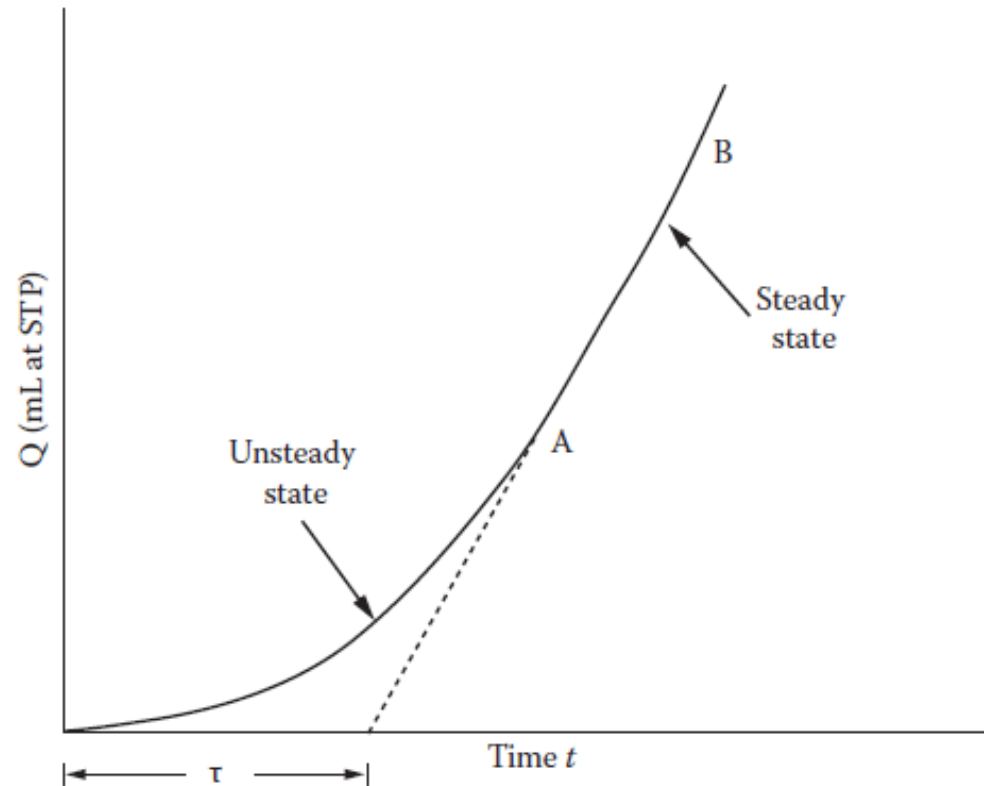
Thus, the amount of gas permeating through the polymer increases linearly with time once the steady-state has been reached, as indicated in Figure.

If the linear portion of the steady-state line AB is extrapolated back to $Q = 0$ where the intercept $t = \tau$, then from Equation.

$$\frac{Dc_1\tau}{X} = \frac{c_1X}{6}$$

$$D = \frac{X^2}{6\tau}$$

Time lag



Typical permeation and time lag curve where Q is the amount of permeant that has permeated as a function of time t and τ is the **time lag**.

All three parameters of interest can be calculated from a single experiment.

- The **permeability coefficient P** is obtained by calculating the steady-state permeation rate Q/t (the slope of the asymptotic line in Figure) and substituting in Equation.
- The **diffusion coefficient D** is obtained from the time lag τ and
- The **solubility coefficient S** is calculated as P/D .

FACTORS AFFECTING THE DIFFUSION AND SOLUBILITY COEFFICIENTS

Pressure

- In the case of the permanent gases, P (permeability coefficient) is independent of the pressure of the diffusing gas.
- This is also true in many instances for other gases and vapors, provided there is no marked interaction between the polymer and the diffusing material.
- However, where there is strong interaction, P (permeability coefficient) is found to be pressure dependent and, in general, it increases as the pressure increases.
- This is due to an increase in D promoted by the plasticizing effect of the sorbed permeant.

Sorption

- The term sorption is generally used to describe the initial penetration and dispersal of permeant molecules into the polymer matrix.
- Sorption behavior has been classified on the basis of the **relative strengths of the interactions between the permeant molecules and the polymer** or between the permeant molecules themselves within the polymer.
- The simplest type of sorption arises when both polymer/permeant and permeant/permeant interactions are weak relative to polymer/polymer interactions; that is, **when ideally dilute solution behavior occurs and Henry's law is obeyed.**
- **S is independent of sorbed concentration at a given temperature** and therefore the sorption isotherm shows a linear dependence of concentration versus vapor pressure (p).

Temperature

The temperature dependence of S over relatively small ranges of temperature can be represented by an Arrhenius-type relationship:

$$S = S_0 \exp\left(-\frac{\Delta H_s}{RT}\right)$$

where ΔH_s is the heat of sorption. For the permanent gases, ΔH_s is small and positive and therefore S increases slightly with temperature. For easily condensable vapors, ΔH_s is negative due to the contribution of the heat of condensation, and thus S decreases with increasing temperature.

The temperature dependence of D can also be represented by an Arrhenius-type relationship as in the following:

$$D = D_0 \exp -\frac{E_d}{RT}$$

Measurement of Permeability

- There are many methods, **four major methods** are used generally.
- For a complete understanding of the principles behind permeability measurements, it is important that the meaning of two terms which are constantly used total and partial pressure of gases in a mixture.
- In a constant volume, the total pressure exerted by the gases present is the sum of the partial pressures of each of the gases (John Dalton in 1801 and known as Dalton's law).

➤ That is, each of the gases of a gas mixture behaves independently of the others. The rate of permeation of a specific gas through a polymeric material is a function of the partial pressure differential of that gas across the material and not of the total pressure difference between the two sides.

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Pressure Increase Method

- The ASTM manometric method for measuring gas transmission rates and permeabilities of flat films is designated D1434.
- It is sometimes referred to an isochoric or constant volume method.
- Test gas (normally at 1 atm) is introduced on one side of the flat film or sheet which is supported with a filter paper and sealed with an O-ring.
- The pressure in the receiving chamber is measured with an open-ended mercury manometer. Provided that the pressure on the high-pressure side remains much larger than that on the low-pressure side, the pressure difference remains essentially constant.
- Through equations relating the geometry of the cell with the rate of pressure rise in the manometer, the gas transmission rate can be calculated.

Volume Increase Method

- In the ASTM standard volumetric method, the change in volume (at constant pressure), due to the permeation of gas through the film, is measured.
- Variable volume permeation cells are used for rapid measurement of relatively high steady-state permeation rates.
- Although the volume increase method is generally simpler to implement, it is less sensitive than the pressure increase method.

- Volumetric methods are used relatively infrequently compared with the use of the pressure increase or concentration increase methods.
- Agreement with other methods is sometimes poor and may be material-dependent.
- The materials being tested often affect the between-laboratory precision. The causes of these variations are not known at this time and it is suggested that this method not be used for referee purposes.

Concentration Increase Method

- In ASTM D3985 Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting Using a Coulometric Sensor, a partial pressure difference across the film with respect to the test gas is created without a difference in total pressure.
- A partial pressure difference is maintained by sweeping one side continuously with the test gas and maintaining an inert gas on the other side into which the test gas diffuses.
- The concentration of the diffusing gas can be measured by chemical analysis, gas chromatography, thermal conductivity or special electrodes.

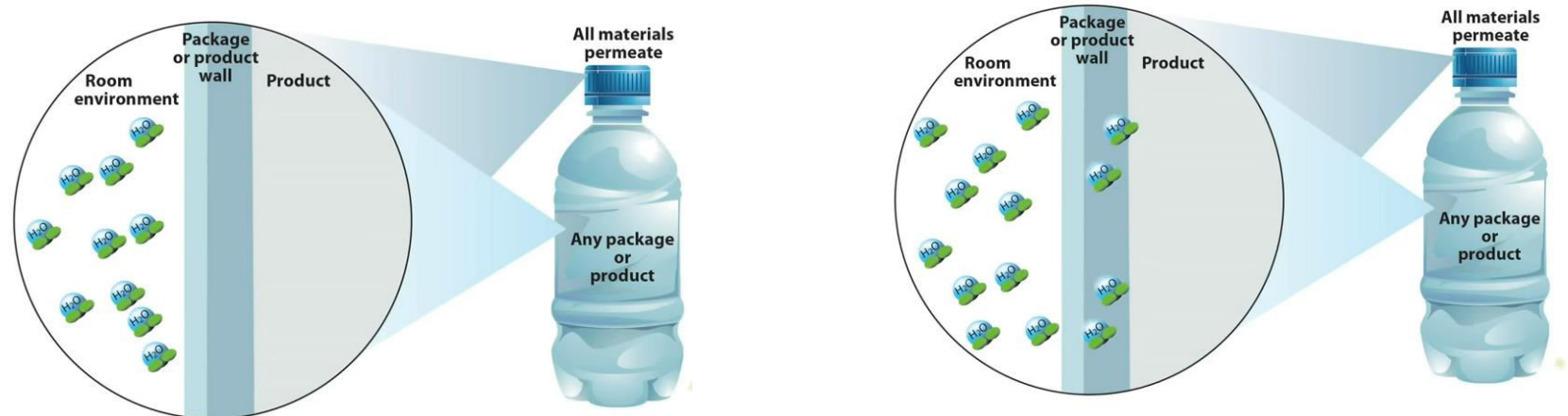
Detector Film Method

- Requires little equipment and is both rapid and accurate, was developed by Holland et al., (1980).
- The basis of the method is a plastic detector film impregnated with a reagent that is sensitive to the gas being measured. The film has an absorption spectrum that changes as the gas or vapor is absorbed (spectrophotometric monitoring).
- The detector film is sealed between two pieces of test film in a simple cell so that the permeation rate of the penetrant gas or vapor can be readily measured.

➤ The O₂ detector consists of a cast film of ethyl cellulose containing dimethylantracene (DMA) and erythrosine. On absorbing blue light, the erythrosine can activate O₂ dissolved in the ethyl cellulose to form singlet O₂, a reactive form of O₂. Singlet O₂ (which has a lifetime of only a few microseconds in the film) diffuses to a neighboring DMA molecule and reacts with it. Thus, the disappearance of DMA (monitored in the UV) is a measure of the O₂ consumed. Since the ethyl cellulose detector is highly permeable to O₂, it is capable of measuring very low rates of O₂ permeation.

Water transmission rate

- (WVTR), often referred to as “moisture vapour transfer rate” is then standard indicator of how easily moisture can permeate a packaging film.
- Its values expressed as g/m^2 and $\text{g}/100 \text{ in}^2$ at 38°C and 98% relative humidity.
- Increasing WVTR values indicate greater permeability and lower ability to keep dry products dry and moist products moist.



Water Vapor Permeability

- The standard method to determine WVTRs is to place a quantity of desiccant in an aluminum dish, which is covered with a sheet of the material being tested and sealed in position with wax.
- The dish is then placed in a closely controlled atmosphere (typically either $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and $75\% \pm 2\%$ RH for temperate conditions, or $38^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and $90\% \pm 2\%$ RH for tropical conditions) and the increase in weight noted as a function of time.
- If the points are plotted out, then they should fall more or less on a straight line because Δp is constant throughout the test.

$$\begin{aligned} \text{WVTR} &= \frac{Q}{At} \\ &= \frac{\text{slope}}{\text{area}} \\ &= \frac{\text{g H}_2\text{O}}{\text{m}^2 \text{ day}} \end{aligned}$$

To convert WVTR into permeance (P/X), it should be divided by the driving force Δp .

Disadvantages

- These methods have several disadvantages, including the length of time needed to make a determination (between 2 and 14 days) and the lower limit of the useful range (about $1 \text{ g m}^{-2} \text{ day}^{-1}$ for a typical packaging film).
- A further disadvantage is that, depending on the desiccant, Δp may not remain constant during the test period.
- In the case of anhydrous CaCl_2 , the partial pressure of water vapor in the dish remains below 2% of the vapor pressure of water at the test temperature during the test, whereas in the case of silica gel, the partial pressure of water sorbed on it increases with coverage.

- In recent years, more rapid methods have been developed. Most of these depend on detecting small changes in the RH of the atmosphere on the dry side of the film.
- Test cells consist of two sections separated by the material under test.
- The lower section contains water to give a saturated atmosphere, while the upper section contains a humidity sensor which is dried by purging with dry air.
- The movement of water vapor through the film raises the RH of the air surrounding the humidity sensor and the time for a given rise can be recorded; from this, the WVTR is calculated.

WVTR Permeability tester



