GAS AND VAPOR PERMEABILITY OF
THE DOUBLE WALL COMPARED TO
SINGLE WALL PLASTIC PACKAGES

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ABSTRACT

GAS AND VAPOR PERMEABILITY OF THE DOUBLE WALL

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By

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A package should be designed for a certain shelf

life, which is the length of time during which a product

has acceptable quality, when stored under conditions of

its usual channels of distribution. Many factors can

affect the shelf life. If we consider only those factors

which can be determined by the package, two of the most

important are the internal gas and vapor concentrations.

The production researcher should tell the package

designer under what conditions the quality of the product

will not be suitable for consumers. (In this paper we

are considering only the internal gas and water vapor

concentration as the factors affecting the shelf life.)

If we assume the internal gas and water vapor

concentrations are dependent only on the conditions at

the time of package closure and the permeability of the

package, for given initial conditions many packages with different permeabilities can be designed. Different packages will result in different shelf lives at different costs. After consultation with the market expert, the best one can be chosen.

The cost is one of the most important factors. This paper introduces a hypothesis and its proofs. Using the hypothesis we can reduce the package material expense. The hypothesis is: the internal, partial pressure of a gas or vapor is smaller in the double wall package as compared with the single wall package until a certain time t_c, if the quality and quantity of the material used, and the temperature, and partial pressure in the packages and between double walls are the same at time $t = 0$. The time t_c:

--is dependent on properties (material, surface area, thicknesses, the space between double walls) of the packages.

--is directly proportional to the difference of the external and internal partial pressure (in packages and between double walls) at time $t = 0$.

The above hypothesis is proved by mathematical proof and also by calculation of an analog computer.

If the needed shelf life is t_s and the limit of the internal partial pressure for the given gas or vapor is p_s, we can design a single wall package which solves

this problem. We assume we did and that package has the minimum material expense.

Following the above, we design a double wall package using the same quality and quantity of the package material and the same sized package. Then internal partial pressure will be p_d at time t_s. Using the hypothesis: if $t_s < t_c$, then $p_d < p_s$. However, the limit for the internal partial pressure is p_s, so p_d may increase to p_s. But p_d increases if the quantity of the package material decreases. The size of the package is fixed, so we can reduce the quantity of package material if we use thinner walls or if we use a smaller space between the double walls. We can do those until $p_d = p_s$. Then we get the needed shelf life in spite of the fact we use less package material.

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INTRODUCTION

A package should be designed for a certain shelf life, which is the length of time during which a product has acceptable quality, when stored under conditions of its usual channels of distribution. If we consider only those factors which can be determined by the package, two of the most important are the internal gas and vapor concentrations. For example, meat changes color, because of oxygen; apples turn to yellow because of carbon dioxide; dry food cannot be used over a certain moisture content; bread is unusable beyond certain moisture levels.

In this work we examine what the differences are in gas or vapor permeability of single and double wall plastic packages. We have developed the equation of the gas and vapor permeability of plastic packages. Using the developed equation we posed seven problems and we solved them. Some of them are mathematical proofs, others are real situations solved by analog computer. To draw conclusions we find a hypothesis, which can be useful for package design, because by using the rule we can save material.

The theory of the gas and vapor permeability of the plastic materials is very well studied. Some excellent

reference books are available (3, 4, 10) and many articles
were written, summarized by Lebovits (11) until 1966.
Much data on gas and water vapor permeability can be found
in the literature but only for sheet material (2, 6, 9,
12, 13, 16, 17). Some data are about the gas permeability
of the real packages (15). More publications are about
water vapor permeability and the relationship between that
and the shelf life (1, 7, 8).

Loudenslagel and Roe (14) wrote about simulation
of the gas permeation in plastic containers by analog
computer. Stannett and Szwarc (18) tried to find a simple
relationship for gas permeability between polymer and gas,
which can be used generally, without real tests. They
tried to calculate one permeability constant from others.

DEVELOPMENT OF THE EQUATION OF THE GAS AND VAPOR
PERMEABILITY OF THE PLASTIC PACKAGES

Mass transport through polymeric materials occurs by activated diffusion. This takes place in three steps. First the permeant dissolves in the permeable membrane on the side of its higher concentration. Then it diffuses through the membrane towards the side of lower concentration, a process which depends on the formation of "holes" in the plastic network due to thermal agitation of the chain segments. Finally the permeant becomes desorbed on the side of the lower concentration. The equation of diffusion is given by Fick's first law:

$$dn = D \frac{\partial c}{\partial \ell} dt \tag{1}$$

n = number of diffused molecules

D = diffusion constant

$\frac{\partial c}{\partial \ell}$ = concentration gradient, which is assumed as constant

t = time

The number of diffused molecules is equal to the diffusion constant times the concentration gradient times time, if the area of the diffusion is unity. The concentration gradient is a constant, if we integrate between l_1, l_2, and c_1 and c_2 it gives

$$\frac{dn}{dt} = D \frac{c_1 - c_2}{l_1 - l_2} \tag{2}$$

$l_1 - l_2 = L$, the thickness of membrane

c_1 = concentration of the gas molecules on one
side of the membrane

c_2 = concentration of the gas molecules on the
other side of the membrane

If the area of the membrane is equal to A,

$$\frac{dn}{dt} = D \frac{c_1 - c_2}{L} A \tag{3}$$

The permeation is a combined process between diffusion and solution, thus the solubility coefficient must be considered, which is given from Henry's law.

$$C = Sp \tag{4}$$

C = concentration of the gas on the surface of the
membrane

S = solubility coefficient

p = partial pressure of the gas in the gas space

After above:

$$\frac{dn}{dt} = DS \frac{c_1 - c_2}{L} A \tag{5}$$

$D \cdot S \equiv P_m$ = permeability constant

$$P_m = \left(\frac{\text{number of diffused mols. x thickness}}{\text{area x time x concentration difference}} \right)$$

$$\frac{dn}{dt} = P_m \frac{c_1 - c_2}{L} A \tag{6}$$

Equation 6 is the equation of the mass permeability of polymeric materials. If we assume ideal gas laws for gases and vapors (which is not completely true, but use of them results in only negligible error) then concentration of the gases and vapors are equal to their partial pressures,

$$\frac{dn}{dt} = P_m \frac{p_1 - p_2}{L} A \qquad (7)$$

p_1 and p_2 are the partial pressures of the gas or vapor on the two sides of the membrane. In the literature the permeability constant is given commonly as:

volume of diffused gas or vapor (STP) x thickness
area x time x pressure difference

P_m = number of mol x $\frac{L}{A \times t \times \Delta P}$

$\bar{P}$ = volume of diff mol (STP) x $\frac{L}{A \times t \times \Delta P}$

$\frac{P_m}{\bar{P}} = \frac{\text{number of mol}}{\text{volume of mol STP}} = \frac{n}{V(STP)}$

V = volume of mol (STP)

$$n = \frac{p_o V}{RT_o} \qquad (8)$$

$$\bar{P}_m = \bar{P} \frac{\frac{p_o V}{RT_o}}{V} = \bar{P} \frac{p_o}{RT_o} \qquad (9)$$

From equation 7 and equation 9,

$$\frac{dn}{dt} = \bar{P} \frac{p_o}{RT_o} \frac{p_1 - p_2}{L} A \qquad (10)$$

p_o = 1 atm

T_o = 273°K

R = Regnard gas constant

Let's take into consideration a real package. We want to know the internal gas or vapor concentration as a function of time (which is equal to partial pressure of gas or vapor). For example:

$p_e(t)$ = the external partial pressure of the gas or vapor

$p_i(t)$ = the internal partial pressure of the gas or vapor

V = volume of the internal gas or vapor space. This is a constant.

If dn molecules go through the wall of packages, the internal partial pressure is changed by dp.

$$n = \frac{pV}{RT} \tag{11}$$

$$dn = \frac{dpV}{RT} \tag{12}$$

From equation 10 and equation 12:

$$\frac{\frac{dpV}{RT}}{dt} = \bar{P} \frac{P_o}{RT_o} \frac{p_e(t) - p_i(t)}{L} \tag{13}$$

$$\frac{dp}{dt} = \bar{P} \frac{A}{VL} P_o \frac{T}{T_o} (p_e(t) - p_i(t)) \tag{14}$$

Equation 14 gives the internal partial pressure of the gas or vapor as a function of time.

We must consider for what condition the equation is true for determination of package life. We must also consider the possible change of every component of the equation as a function of time, temperature and pressure.

There may not be any chemical reactions between the gases and solids (the material of the package or the packaged product) or liquids (the packaged product). The commonly considered gases and vapor relatively inert under usual conditions and package materials ordinarily are chemically inactive.

The permeation of gases or vapors are independent, so the equation is true for each gas or vapor separately.

We assume the velocity of the gases or vapors is zero inside and also outside of the package.

The time required to reach steady state is negligible compared to the storage time.

The package is faultless. There is no leakage, no damage, no mechanical distortion.

The sign of an infinitisimally small change of the internal pressure (dp) depends on the direction of the permeation. p_i is always the internal partial pressure of the gas or vapor. The sign of dp_i is positive, if the direction of permeation is from outside to inside of the package.

The infinitesimally short time change (dt) is practically zero as compared to the storage time.

The area of permeation (A) is the area that gas or vapor can go through. The area is constant for all time, temperature, and pressure.

The thickness of package wall (L) must be the same everywhere, which for a curved surface is sometimes not true. To correct for this we might use average thickness. The change of thickness may be a function of time, for example degradation. It might be estimated, but usually this is not necessary. The thickness is independent of time, temperature and pressure.

The volume of gas space (V) is only the actual gas or void space. For the package of a very porous material we might consider the volume of the pores. The volume of the gas space is independent of time, temperature and pressure.

$\bar{P}$ is the permeability constant.
$$\bar{P} \equiv D \cdot S$$

The diffusion constant is assumed independent of the concentration of the permeant in the membrane. The solubility coefficient is also assumed independent of the pressure of the permeant in the phase in equilibrium with the membrane. In this case the permeability constant is independent of the pressure. The temperature dependence of D and S is expressed by Arrhenius type equations.

$$D = D_o \exp(-E_d/RT) \qquad (15)$$

$$S = S_o \exp(-\Delta H_s/RT) \qquad (16)$$

E_d = activation energy for the diffusion process

H_s = the heat consumed on dissolving a mole of permeant in the membrane

R = Regnard gas constant

$$\bar{P} \equiv DS = D_o \exp(-E_d/RT) \; S_o \exp(-\Delta H_s/RT) \qquad (17)$$

$$\bar{P}_o = D_o S_o \qquad (18)$$

$$E_p = E_d + \Delta H_s \qquad (19)$$

$$\bar{P} = \bar{P}_o \exp(-E_p/RT) \qquad (20)$$

E_p and $\bar{P}_o$ can be determined from two permeability constants, which were measured at different temperatures. The permeability constant is independent of time and pressure.

p_o is 1 atm

T_o is 273°K

T is the temperature at any time. This may be changed by function of time.

p_e is the external partial pressure of the gas or vapor. This is constant or zero (N_2, O_2, CO_2) or function of time and temperature.

p_i is the internal partial pressure of the gas or vapor. This is a function of temperature.

$$p_i = p_{io} \frac{T}{273} \tag{21}$$

T = temperature $°K$

p_{io} = internal partial pressure at $273°K$

The internal partial pressure of gas or vapor is changed by time.

Then equation of gas or vapor permeability of the plastic package is

$$\frac{dp_i}{dt} = \bar{P}_o \, e^{-\frac{E_p}{RT(t)}} \, \frac{T(t)}{T_o} \, p_o \, \frac{A}{VL} \, (p_e(t) - \frac{p_{io}(t)T(t)}{273}) \tag{22}$$

PROBLEM 1

We have to design a package with volume V. The package has no product and is filled with N_2 gas. The oxygen concentration is zero at time t = 0. At t_f time the internal partial pressure of the oxygen may not be more than p_f in the closed package. (The increase of the internal partial pressure of the oxygen is caused by oxygen permeation only.) The temperature is constant T_f°K. The external gas is air.

Requirement: The material expense should be a minimum.

Solution: After we have decided the shape of the package we can calculate the surface area A of that, from the volume of the package. We can use the equation of the gas and vapor permeability of the plastic packages, equation 22.

$$\frac{dp_i}{dt} = \bar{P}_o \exp(-\frac{E_p}{RT(t)}) \frac{T(t)}{T_o} P_o \frac{A}{VL} (p_e(t) - \frac{p_{io}(t)T(t)}{273}) \quad (23)$$

T is constant and equal to T_f. Using equation 19,

$$\bar{P}_{T_f} = \bar{P}_o \exp(-E_p/RT_f) \quad (24)$$

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$\bar{P}_{T_f}$ is constant. p_o; T_o are constant also. After above,

$$\frac{dp_i}{dt} = k \frac{A}{VL} (p_e(t) - p_i(t)) \qquad (25)$$

where

$$k = \bar{P}_{T_f} \cdot \frac{T_f}{T_o} p_o \qquad (26)$$

and

$$p_i(t) = \frac{p_{io}(t) T_f}{273} \qquad (27)$$

The external partial pressure of the oxygen is constant P, because the external gas is air.

$$\frac{dp_i}{dt} = k \frac{A}{VL} (P - p_i(t)) \qquad (28)$$

Let's integrate the equation 28 between o and t, and p(o) and p(t).

$$p_i(t) = P[1 - \exp(-k \frac{A}{VL} t)] + p_i(o) \exp(-k \frac{A}{VL} t) \qquad (29)$$

where $p_i(o)$ is the internal partial pressure of the oxygen at t = 0 time. But $p_i(o) = 0$.

$$p_i(t) = P[1 - \exp(-k \frac{A}{VL} t)] \qquad (30)$$

Since $p_i(t)$ may not be larger than p_f at time $t = t_f$ we can use

$$p_i(t_f) = p_f \qquad (31)$$

Using equation 29 and equation 30,

$$P_f = P[1 - \exp(-k \frac{A}{VL} t_f)] \qquad (32)$$

A and V are constants. So from equation 32,

$$\frac{\ln (1 - \frac{P_f}{P})}{\frac{A}{V} t_f} = \frac{k}{L} \qquad (33)$$

Using equation 26 and equation 33,

$$\frac{V T_o \ln (1 - \frac{P_f}{P})}{A_1 T_f P_o} = \frac{\bar{P} T_f}{L} \qquad (34)$$

If we assume the expense of the process of package making is independent of the quality of the material used, then the minimum material expense will be obtained by use of the minimum material. The quantity of the material is equal to surface area times thickness. The surface area is fixed, so minimum thickness results in minimum quantity of material.

From the literature we can pick the oxygen permeability constants of different materials. (We can calculate the P_{T_f} from two different oxygen permeability constants, which were measured at two different temperatures. Using a semi-log graph, where the permeability constants are plotted against reciprocal of absolute temperature, we can draw a straight line through the two points. We can read the oxygen permeability constant for $T_f °K$ temperature.)

Using equation 34 we can see the left side of the equation is constant B, so

$$L = \frac{\bar{P}_{T_f}}{B} \qquad (35)$$

From $\bar{P}_{T_f}$ and B we can calculate L.

$$N = L \times A \times U \qquad (36)$$

Where N is the cost of material, U is the unit price. If we make this calculation for many materials, we can find the minimum material expense.

Conclusion: If the material, M, has an oxygen permeability constant $\bar{P}_m$ at temperature T_f, the wall thickness should be L_m for a given shelf life problem. We cannot reduce the material expense, because in equation 34 everything is fixed.

PROBLEM 2

How does the internal partial pressure of the oxygen change as a function of time for a single wall package compared with a double wall package? Assume that the internal volume of the package and quantity and quality of the package material are the same, the temperature is constant, and the external gas is air.

a. The internal partial pressure of oxygen is zero at time $t = 0$ for both packages and between double wall.

b. The internal partial pressure of oxygen is the same for both packages, and is not zero at time $t = 0$.

Solution: The single wall package has volume V_1, surface area A_1 and wall thickness L_1. The double wall package can be considered as two packages. The smaller package has a volume V_1, area A_1 and wall thickness L_3. The larger package has a volume V_2 (which is equal to the full volume minus the volume of the smaller package); surface area A_2 and wall thickness L_2. The quantity and quality of material is the same; so

$$A_1 L_1 = A_1 L_3 + A_2 L_2 \qquad (37)$$

Using equation 22 for single wall package,

$$\frac{dp_i}{dt} = \bar{P}_o \exp\left(-\frac{E}{RT}\right) \frac{T}{T_o} P_o \frac{A}{V_1 L_1} P_{(e)}(t) - p_i(t)) \tag{38}$$

but $p_e(t)$ is constant because the external gas is air. Because T is constant

$$\frac{dp_i}{dt} = k \frac{A_1}{V_1 L_1} (P - p_i(t)) \tag{39}$$

where $\bar{P}_o \left(\exp - \frac{E}{RT}\right) \frac{T}{T_o} P_o = k \tag{40}$

Using equation 25 for double wall package,

$$\frac{dp_i^*}{dt} = k \frac{A_1}{V_1 L_3} (p_m(t) - p_i^*(t)), \tag{41}$$

where $p_m(t)$ is the internal partial pressure of the oxygen between the double wall.

Some gas molecules will go into the double walls from outside.

$$\frac{dp_m^1}{dt} = k \frac{A_2}{V_2 L_2} (P - p_m(t)) \tag{42}$$

and some gas molecules will leave from between double walls and they move into the smaller package at the same time.

$$\frac{dp_m^2}{dt} = k \frac{A_1}{V_2 L_3} (p_i^*(t) - p_m(t)) \tag{43}$$

or

$$\frac{dp_m^2}{dt} = -k \; \frac{A_1}{V_2 L_3} \; (p_m(t) - p_i^*(t)) \qquad (44)$$

$$\frac{dp_m}{dt} = \frac{dp_m^1}{dt} + \frac{dp_m^2}{dt} \qquad (45)$$

Combination of the equation 42, equation 43 and equation 45,

$$\frac{dp_m}{dt} = k \; \frac{A_2}{V_2 L_2} \; (P - p_m(t)) - k \; \frac{A_1}{V_2 L_3} \; (p_m(t) - p_i^*(t)) \qquad (46)$$

k is always the same constant, because the same material and temperature are used.

Let's say:

$$k \; \frac{A_1}{V_2 L_3} \; (p_m(t) - p_i^*(t)) = Z(t) \qquad (47)$$

$Z(o) = 0$ because of the same initial condition.

$Z(\infty) = 0$ because after $t = \infty$, p_m and p_i^* will be equal to P.

$Z(t) > 0$ $p_m(t)$ is always larger than $p_i^*(t)$.

If we assume $Z(t) = 0$, then equation 46 will be:

$$\frac{dp_m^+}{dt} = k \; \frac{A_2}{V_2 L_2} \; (P - p_m(t)) \qquad (48)$$

but, because $Z(t) \geq 0$,

$$\frac{dp_m^+}{dt} \geq \frac{dp_m}{dt} \qquad (49)$$

The combination of equation 48 and equation 49,

$$\frac{dp_m}{dt} \geq k \frac{A_2}{V_2 L_2} (P - p_m(t)) \qquad (50)$$

If we integrate the equation 50 between 0 and t, $p_m(o)$ and $p_m(t)$,

$$p_m(t) \leq P [1-\exp(-k \frac{A_2}{V_2 L_2} t)] + p_m(o) \exp(-k \frac{A_2}{V_2 L_2} t) \qquad (51)$$

if $p_m(o) = 0$ (situation a),

$$p_m(t) \leq P[1-\exp(-k \frac{A_2}{V_2 L_2} t)] \qquad (52)$$

For $p(o) = 0$, $p_i^*(o) = 0$, $p_m(o) = 0$ (situation a) we can combine equation 41 and equation 52.

$$\frac{dp_i^*}{dt} \leq k \frac{A_1}{V_1 L_3} [P (1-\exp(-k \frac{A_2}{V_2 L_2} t)) - p_i^*(t)] \qquad (53)$$

or

$$\frac{dp_i^*}{dt} \leq k \frac{A_1}{V_1 L_3} (P - p_i^*(t) - P \exp(-k \frac{A_2}{V_2 L_2} t)) \qquad (54)$$

Compare equation 54 with equation 39.

$$\frac{dp_i}{dt} = k \frac{A_1}{V_1 L_1} (P - p_i(t))$$

$k \frac{A_1}{V_1 L_3} > k \frac{A_1}{V_1 L_1}$ because $L_1 > L_3$. But until a certain time

$- P \exp(-k \frac{A_2}{V_2 L_2} t) k \frac{A_1}{V_1 L_3}$ is larger than the difference

which is caused by $L_1 > L_3$. It can be seen that the certain

time t_c is dependent on the constants. If L_3 and $k \frac{A_2}{V_2 L_2}$

decrease, then t_c increases. It can be proven if V_2 and A_2

are increasing, $\frac{A_2}{V_2}$ is decreasing. In this way we need

large L_3, A_2, V_2 and L_2. Equation 37 gives a relationship

among them for problem 2.

$$A_1 L_1 = A_1 L_3 + A_2 L_2$$

Since A_1 and L_1 are fixed, so increase of all

factors (A_2, L_2, L_3) is impossible, so we can suppose we

have to find an optimum value for A_2, L_2, L_3 which gives

the longest t_c.

For $p_i(o) = p_i^*(o) = p_m(o) \neq 0$ (situation b) we

can combine equation 41 and equation 51.

$$\frac{dp_i^*}{dt} \leq k \frac{A_1}{V_1 L_3} [P - p_i^*(t) - (P - p_m(o)) \exp(-k \frac{A_2}{V_2 L_2} t)] \quad (55)$$

Compare equation 55 with equation 39 and it can be

seen if $p_i(o) = p_i^*(o) = p_m(o)$ increase, the time t_c de-

creases and approaches zero, but never can reach that if

$p_i(o) = p_i^*(o) = p_m(o) < P$, because we can always find time

when the second part of the right side of equation 55 is

larger than the difference which was caused by $L_1 > L_3$.

Conclusion: The internal partial pressure of the oxygen is always smaller in the double wall package compared with single wall package until a certain time t_c, if the quality and quantity of the used material are the same and the temperature and partial pressure in the packages and between double walls are the same. The time t_c is dependent on the properties of the package (material, surface area, volume, wall thicknesses, the space between double walls), and the internal partial pressure of the oxygen in the packages and between double walls at time $t = 0$. The time t_c can not be zero ever, if the external partial pressure of the oxygen is higher than the internal partial pressure of the oxygen at time $t = 0$.

PROBLEM 3

This is the same as problem 1, but uses a double wall package and results of the problem 2. $t_f < t_c$.

Solution: If $t_f < t_c$, then $\dfrac{dp_i^*}{dt} < \dfrac{dp_i}{dt}$ (from problem 2). But $p_i(o) = p_i^*(o)$, so

$$p_i^*(t_f) < p_i(t_f)$$

But $p_i(t_f) = p_f$, so $p_i^*(t_f) < p_f$.

The internal partial pressure may not be more than p_f, so can be p_f. So $p_i^*(t_f)$ may increase to p_f. But $p_i^*(t_f)$ is increasing, then we use less material. We can use always less and less material until $p_i^*(t_f) = p_f$. In this way we can reduce the quantity of materials. We can do this two ways, using thinner L_2 and L_3, or using smaller A_2, which is given by smaller V_2.

Conclusion: If the needed shelf life time t_f is shorter than t_c, then by using the double wall package, we can save package materials.

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PROBLEM 4

We have a cylindrical package. The height of the package is equal to the diameter. The package is empty, and it is filled up with nitrogen gas. The material is polyethylene. The package is closed and the oxygen concentration is zero at time t = 0. The diameter of the package is 10 cm. The temperature is constant 25°C. The external gas is air.

The oxygen permeability constant of the polyethylene at 25°C is 0.66 $\dfrac{cm^3 \; x \; mm}{cm^2 \; x \; month \; x \; atm}$.

The wall thickness is 1 mm. What will the internal partial pressure of the oxygen be at 0.25, 0.5, 1.0 and 1.5 months?

Solution: Using the equation of the gas permeability of the packages, equation 22,

$$\frac{dp_i}{dt} = \bar{P} \; \frac{T}{T_o} \; P_o \; \frac{A}{VL} \; (p_e(t) - p_i(t))$$

$$\bar{P} = 0.66 \; \frac{cm^3 \; x \; cm}{cm^2 \; x \; month \; x \; atm}$$

$$T = 298°K$$

$$T_o = 273°K$$

$p_e(t) = 0.21$. The oxygen concentration is a constant 21% in the air.

$$p_o = 1 \text{ atm}$$

After the above,

$$\frac{dp_i}{dt} = 0.734 \frac{A}{VL} (0.21 - p_i(t))$$

D = diameter 10 cm

H = weight of package 10 cm

$$A = \frac{2D^2\pi}{4} + D\pi H \tag{56}$$

but D = H

$$A = \frac{3D^2\pi}{2} \tag{57}$$

$$V = \frac{D^2\pi \cdot H}{4} = \frac{D^3\pi}{4} \tag{58}$$

Using equation 58 and equation 57,

$$\frac{A}{V} = \frac{6}{D} \tag{59}$$

D = 10 cm, so $\frac{A}{V} = 0.6$

After the above,

$$\frac{dp_i}{dt} = 0.440 (0.21 - p_i(t))$$

To solve this problem we can make a simple analog computer circuit in Figure 1.

Because of $p(o) = 0$, the initial condition is 0. The results are given in Table 1.

Conclusion: The internal partial pressure of the oxygen reaches 50% of the external partial pressure after 1.5 months.

Table 1. Internal partial pressure of the oxygen in the single wall package at different times.

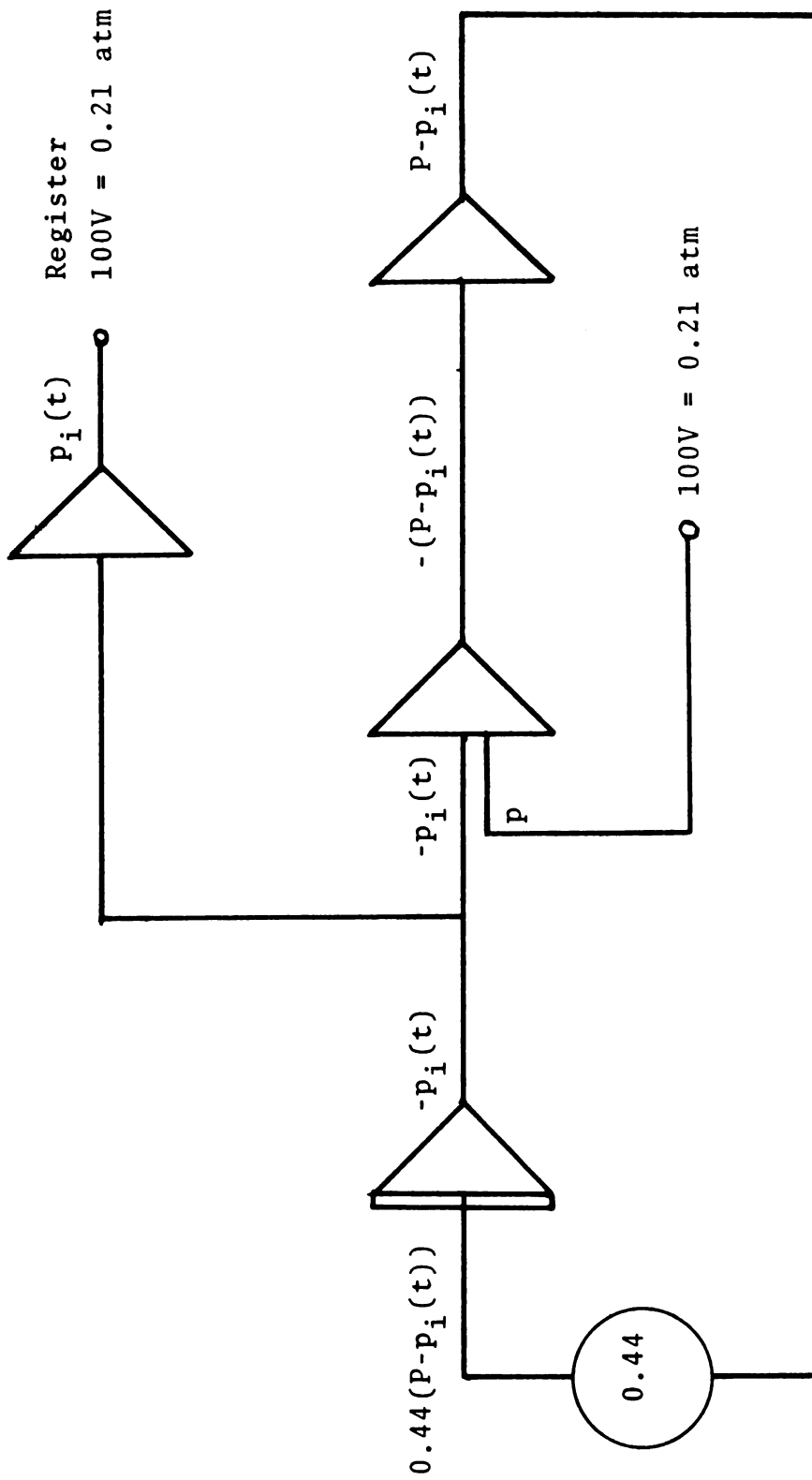|	Time (months)			
	0.25	0.5	1.0	1.5
Internal partial pressure of the oxygen (atm)	0.022	0.042	0.076	0.104

Figure 1. Analog computer circuit to simulate the internal partial pressure change of the oxygen of the single wall package as function of time.

PROBLEM 5

The problem is the same as problem 4, but we use double wall package instead of single. The quantity and quality of the used material are the same. The partial pressure of the oxygen is zero between double wall t = 0 time. The conditions are the same. What will be the internal partial pressure of the oxygen at 0.25, 0.5, 1.0 and 1.5 months?

Solution: The double wall package consists of two single packages. Symbols are the same as in problem 2.

$$D_2 = XD_1 \quad \text{and} \quad H_2 = XH_1$$

From equation 57,

$$A_1 = \frac{3D_1^2 \pi}{2} \qquad\qquad A_2 = \frac{3D_2^2 \pi}{2}$$

But $D_2 = XD_1$, so $A_2 = \frac{3X^2 D_1^2 \pi}{2}$

$$V_1 = \frac{D_1^3 \pi}{4}$$

$$V_2 = \frac{D_2^3 \pi}{4} - V_1 = \frac{X^3 D_1^3 \pi}{4} - \frac{D_1^3 \pi}{4} = (X^3 - 1) \frac{D_1^3 \pi}{4}$$

26

Using equation 41 and equation 46,

$$\frac{dp_i^*}{dt} = k \frac{A_1}{V_1 L_3} (p_m(t) - p_i^*(t))$$

$$\frac{dp_m}{dt} = k \frac{A_2}{V_2 L_2} (P - p_m(t) - k \frac{A_1}{V_2 L_3} (p_m(t) - p_i^*(t))$$

k = 0.734 (from problem 4).

The used material should be the same as in problem 4.

$$A_1 L_1 = A_1 L_3 + A_2 L_2 \tag{60}$$

or

$$L_1 = L_3 + \frac{A_2}{A_1} L_2 \tag{61}$$

L_1 = 1 mm (from problem 4)

$$A_1 = \frac{3D_1 \pi}{2} \qquad\qquad A_2 = \frac{3X^2 D_1^2 \pi}{2}$$

After the above,

$$1 = L_3 + X^2 L_2 \tag{62}$$

Because D_1 = 10 cm

$$k \frac{A_1}{V_1 L_3} = \frac{0.734 \cdot 0.6}{L_3} = \frac{0.44}{L_3}$$

$$k \frac{A_2}{V_2 L_2} = \frac{0.734 \cdot 0.6 \ X^2}{L_2 (X^3 - 1)} = \frac{0.44 \ X^2}{L_2 (X^3 - 1)}$$

$$k \frac{A_1}{V_2 L_3} = \frac{0.734 \cdot 0.6}{(X^3 - 1) L_3} = \frac{0.44}{(X^3 - 1) L_3}$$

$$\frac{dp_i^*}{dt} = \frac{0.44}{L_3} (p_m(t) - p_i^*(t)) \tag{63}$$

$$\frac{dp_m}{dt} = \frac{0.44 \, X^2}{L_2(X^3-1)} (P - p_m(t)) - \frac{0.44}{(X^3-1)L_3} (p_m(t) - p_i^*(t)) \tag{64}$$

where P is 0.21 (the partial pressure of the oxygen in the air).

Using different ratios, X of the diameters, we can calculate the constants.

We can solve this problem by an analog computer circuit in Figure 2. Because $p_i^*(o) = p_m(o) = 0$, the initial conditions are 0.

Choosing X = 1.05, 1.10, 1.2, and using L_2 = 0.3, 0.4, 0.5, 0.6 mm after calculation of constants and use of analog computer circuit, Figure 2, the results are given in Table 2.

Conclusion: The internal partial pressure of the oxygen is smaller than in the single wall package (problem 4) until a certain time t_c. This way the conclusion of problem 2 is proved. Using larger ratios X of the diameters time t_c increases. If the ratio X of the diameters is constant, time t_c increases if the ratio of wall thicknesses approaches 1.
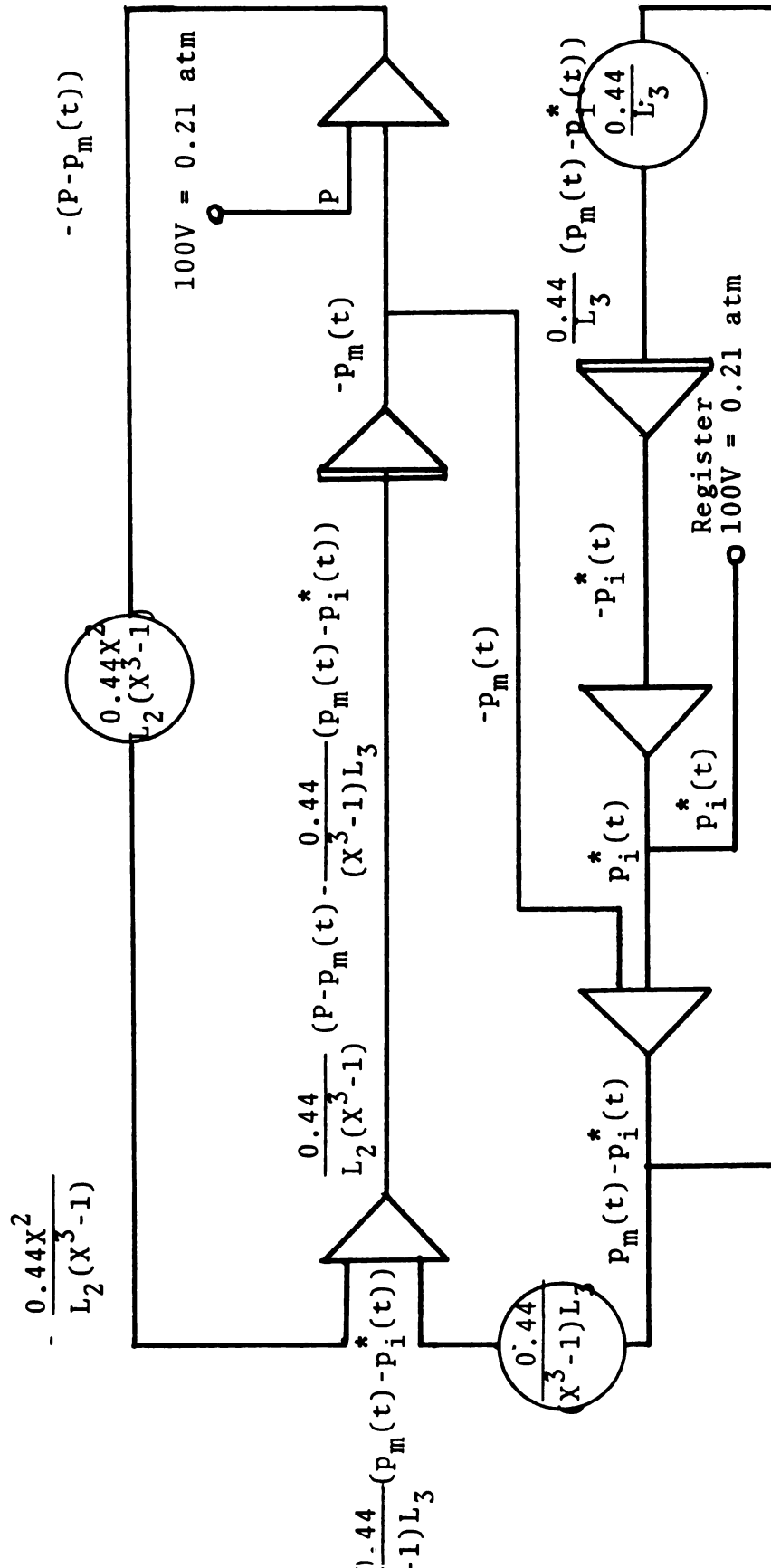
Figure 2.   Analog computer circuit to simulate the internal partial pressure change of the double wall package as function of time.

Table 2. Internal partial pressure of the oxygen for the double wall package at different times, different wall thicknesses and different ratios of the diameters.

X	L_3 (mm)	L_2 (mm)	Internal partial pressure of the oxygen at time (in atm)			
			0.25 month	0.5 month	1.0 month	1.5 month
1.05	0.685	0.300	0.017	0.038	0.074	0.103
1.05	0.580	0.400	0.016	0.038	0.076	0.107
1.05	0.475	0.500	0.018	0.039	0.075	9.105
1.05	0.370	0.600	0.017	0.039	0.076	0.103
1.10	0.637	0.300	0.014	0.034	0.072	0.104
1.10	0.516	0.400	0.014	0.034	0.073	0.105
1.10	0.395	0.500	0.014	0.036	0.073	0.105
1.10	0.274	0.600	0.015	0.038	0.075	0.107
1.20	0.856	0.100	0.014	0.036	0.072	0.101
1.20	0.568	0.300	0.011	0.032	0.069	0.104
1.20	0.424	0.400	0.010	0.030	0.068	0.103
1.20	0.280	0.500	0.013	0.034	0.073	0.107
1.20	0.136	0.600	0.015	0.037	0.075	0.109
1.20	0.092	0.700	0.017	0.039	0.076	0.110

PROBLEM 6

Everything is the same as in problem 5. How will the results change:

a. If we use only 90% of the material decreasing A_2?

b. If we use only 96%, 93%, 90% of the material decreasing L_2 and L_3?

Solution:

a. Using equation 54,

$$L_1 = L_3 + \frac{A_2}{A_1} L_2, \text{ but } \frac{A_2}{A_1} = X^2.$$

For equation 55,

$$L_1 = L_3 + X^2 L_2$$

$$X^2 = \frac{L_1 - L_3}{L_2}$$

but

$$L_1^* = 0.9 \ L_1$$

$$X^{*2} = \frac{L_1^* - L_3}{L_2}$$

$$X^{*2} = \frac{0.9 \ L_1 - L_3}{L_2}$$

If L_2 and L_3 are given, we can calculate X^* and X^* can be used in equation 63 and equation 64 instead of X. To do this calculation for

L_2	0.400	0.500	0.600
L_3	0.424	0.280	0.136

and using an analog computer in Figure 2, the results are shown in Table 3.

    b. Using equation 62,

$$L_1 = L_3 + X^2 L_2$$

If we use Y% of the material (Y = 90, 93, 96), $YL_1 = YL_3 + YX^2 L_2$, but X is constant, so if we multiply L_3 and L_2 by Y we will use Y% of the material.

Using YL_3 and YL_2 in equation 63 and equation 64 instead of L_3 and L_2, we can get the answer using analog computer. The results are in Table 4 for X = 1.2 and L_2 = 0.4 and 0.500, L_3 = 0.424 and 0.280.

Conclusion: To reduce the quantity of the package material, time t_c decreases. The time t_c decreases at a slower rate if the quantity of package material is reduced in wall thickness, and t_c decreases at a faster rate than noted above if the quantity of material is reduced by decreasing the space between the double walls.

Table 3. Internal partial pressure of the oxygen in the double wall package using 90%, 93%, 96% of original quantity of the package material (wall thicknesses decreased).

X	L_3 (mm)	L_2 (mm)	Internal partial pressure of the oxygen at time (in atm)			
			0.25 month	0.5 month	1.0 month	1.5 month
1.2	0.407	0.384	0.013	0.035	0.075	0.109***
1.2	0.395	0.372	0.014	0.036	0.079	0.111**
1.2	0.383	0.360	0.015	0.038	0.082	0.115*
1.2	0.269	0.480	0.014	0.037	0.078	0.115***
1.2	0.262	0.465	0.015	0.039	0.082	0.119**
1.2	0.255	0.450	0.016	0.043	0.087	0.122*

* = 90%   ** = 93%   *** = 96%

Table 4. Internal partial pressure of the oxygen in the double wall package using 90% of original quantity of package material (ratios of diameters decreased)

X	L_3 (mm)	L_2 (mm)	Internal partial pressure of the oxygen at time (in atm)			
			0.25 month	0.5 month	1.0 month	1.5 month
1.104	0.424	0.400	0.022	0.040	0.084	0.116
1.090	0.280	0.500	0.020	0.045	0.088	0.126

PROBLEM 7

How are results of problem 4 and problem 5 changed if $p_i(o) = p_m(o) = p_i^*(o) \neq 0$?

Solution: Using the analog computer circuits in Figure 1 and Figure 2, we use initial conditions for the integrations. The results are in Table 5 for

$$p_i(o) = p_m(o) = p_i^*(o) = 0.042; \ 0,064; \ 0.084; \ 0.105;$$
$$0.147; \ 0.168 \text{ atm}. \quad X = 1.2; \ L_2 = 0.4; \ L_3 = 0.424.$$

Conclusion: Time t_c decreases if $p_i(o) = p_m(o) = p_i^*(o)$ increase.

Table 5. Internal partial pressure of the
oxygen in the double wall package
at different initial conditions
and at different times.

Initial condition (atm)	Wall of the Package	Internal partial pressure of the oxygen at time (in atm)		
		0.5 month	1.0 month	1.5 month
0.042	Single	0.078	0.102	0.127
0.064	"	0.092	0.117	0.137
0.084	"	0.111	0.131	0.148
0.105	"	0.128	0.145	0.158
0.147	"	0.166	0.171	0.179
0.168	"	0.176	0.181	0.189
0.042	Double	0.067	0.100	0.129
0.064	"	0.084	0.113	0.139
0.084	"	0.103	0.128	0.150
0.105	"	0.119	0.143	0.160
0.147	"	0.155	0.169	0.181
0.168	"	0.172	0.183	0.191

SUMMARY AND CONCLUSIONS

If we evaluate the solutions and results of the seven problems, we see the following:

The internal partial pressure of a gas or vapor is always smaller in the double wall package compared with single wall package until a certain time t_c if the quality and quantity of the used material are the same, and the temperature and partial pressure in the packages and between double walls are the same at time t = 0.

Time t_c increases if the space between double walls increases.

For a given double wall package time t_c is longer as the ratio of the wall thicknesses approaches 1.

The time t_c decreases at a slower rate if the quantity of material is reduced in wall thickness and t_c decreases at a faster rate than noted above if the quantity of material is reduced by decreasing the space between the double walls.

The time t_c is inversely proportional to the internal partial pressure at time t = 0.

The time t_c can be very small but cannot be zero ever if the external partial pressure is higher than the internal partial pressure at time t = 0.

If the required shelf life for a package (considering internal partial pressure) is shorter than time t_c using a double wall package material can be saved.

After above we can formulate the hypothesis: The internal partial pressure of a gas or vapor is always smaller in the double wall package compared with single wall package until a certain time t_c, if the quality and quantity of the material used and the temperature are the same and partial pressure in the packages and between double walls are the same at time t = 0. The time t_c

--is dependent on properties of the packages (material, volume, surface area, wall thickness, the space between double walls).

--is directly proportional to the difference of the external and internal partial pressure (in packages and between the double walls) at time t = 0.

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