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Conference**

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Permeation and Measurement Techniques

Presented by:

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WHY A PACKAGE ???

- CONTAINMENT
- PROTECTION
- MARKETING

ALL
MATERIALS
PERMEATE!!!

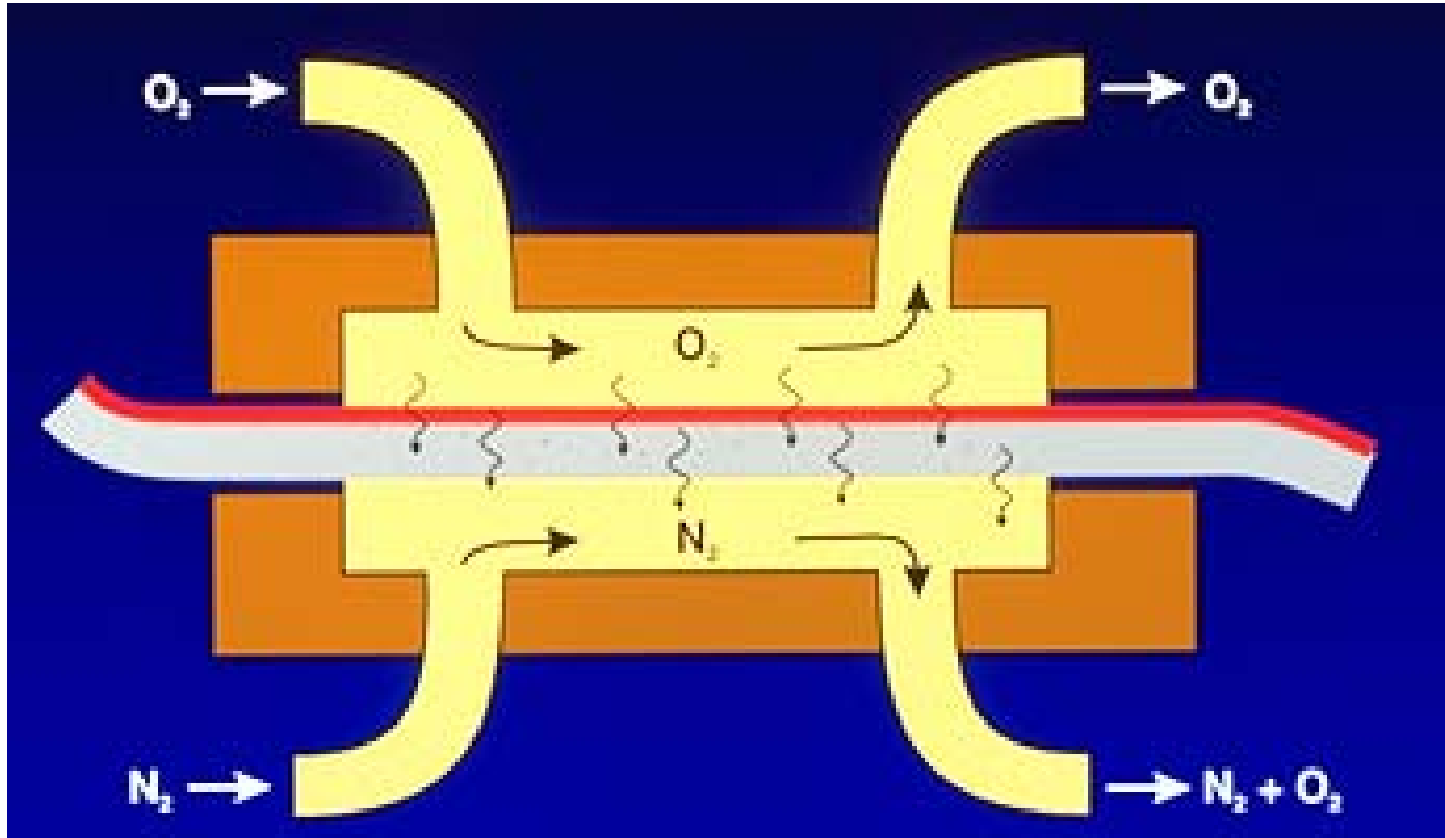
Permeation basics

- Permeation is simply the flux of molecules through a material normalized to the pressure gradient
- Units of permeation “explain” the mechanism:

– SI units

$$\frac{\text{volume of gas at STP} \rightarrow \text{cm}^3 (273.15K; 1.013 \times 10^5 Pa) \times \text{material thickness} \rightarrow \text{cm}}{\text{area} \rightarrow \text{cm}^2 \times \text{time} \rightarrow s \times \text{pressure drop, driving force} \rightarrow Pa}$$

Isostatic Permeation Methodology (Oxygen transmission rate test)



Permeation basics

Permeation rate $\frac{cc \times mil}{m^2 \times day \times atm}$

Transmission rate $\frac{cc}{m^2 \times day}$

History of Permeation Theory

- **1829:** Graham observed permeation of CO₂ into a wet pig's bladder
- **1831:** Mitchell discovered balloons collapse at different rates when filled with different gases
- **1855:** Fick proposed his law of mass diffusion as by analogy with Fourier's law for heat conduction and Ohm's law for electrical conduction
- **1855:** Graham postulated "colloidal diffusion", dissolution of the penetrant followed by transmission of the dissolved species through the membrane
- **1879:** Von Wroblewski observed Henry's Law with gases in rubber and combined this with FICK'S Law to obtain the relationship between permeation and the area and thickness of the membrane.

Solution-diffusion mechanism (Graham's *colloidal diffusion*)

The gas is sorbed at the entering face and dissolved

The dissolved penetrant molecules then diffuse through the membrane and

Desorb at the exit face.

Permeation

The relationship between the rate of permeation
And the concentration gradient is embodied in Fick's
First law:

$$J = -D \frac{\partial C}{\partial x}$$

Where J is the flux per unit area of permeant through the polymer, D is the diffusion coefficient, and $\delta c/\delta x$ is the concentration gradient of the permeant across a thickness δx

Permeation

Fick's second law:

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

Applies under circumstances where diffusion is limited to the x-direction and D is independent of concentration

Pasternak's Solution of Fick's Law

$$F(x) = -D(dc/dx)$$

Assumptions:

The diffusion coefficient D is not a function of the concentration

The surface concentration is proportional to the pressure of the permeant

The swelling of the polymer is negligible.

Pasternak's Solution of Fick's Law

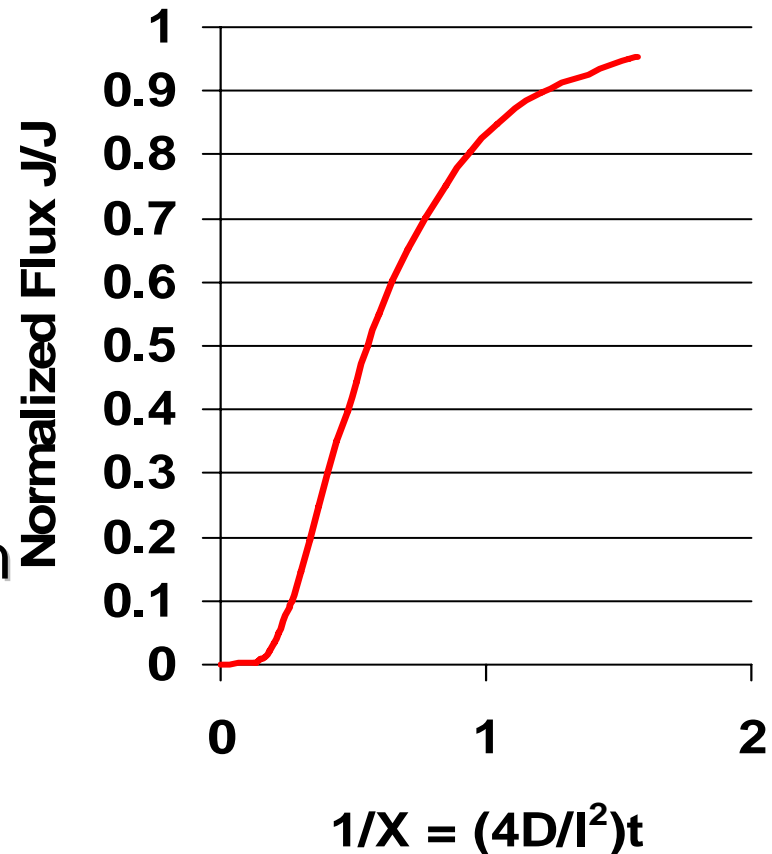
Boundary conditions:

$c = 0$	$x = 0$	$t = 0$
$c = 0$	$0 \leq x \leq l$	$t = 0$
$c = c_f$	$x = 0$	$t > 0$
$c = 0$	$x = l$	$t \geq 0$
$c = c_f(l-x)/l$	$0 \leq x \leq l$	$t = \infty$

Pasternak's Solution of Fick's Law

$$\frac{\Delta J}{\Delta J_{\infty}} = \left(\frac{4}{\sqrt{\pi}} \right) \sqrt{X} \exp \{ - X \}$$

Theoretical permeation
curve for constant diffusion
coefficient



Permeability

- Permeability can be defined as the product of the solubility coefficient and the diffusion coefficient

$$P = S \times D$$

Solubility Diffusion
coefficient coefficient

- Generally, P and S can be directly measured and D can be calculated.
- However, there are indirect methods for measuring D as well.

Diffusion

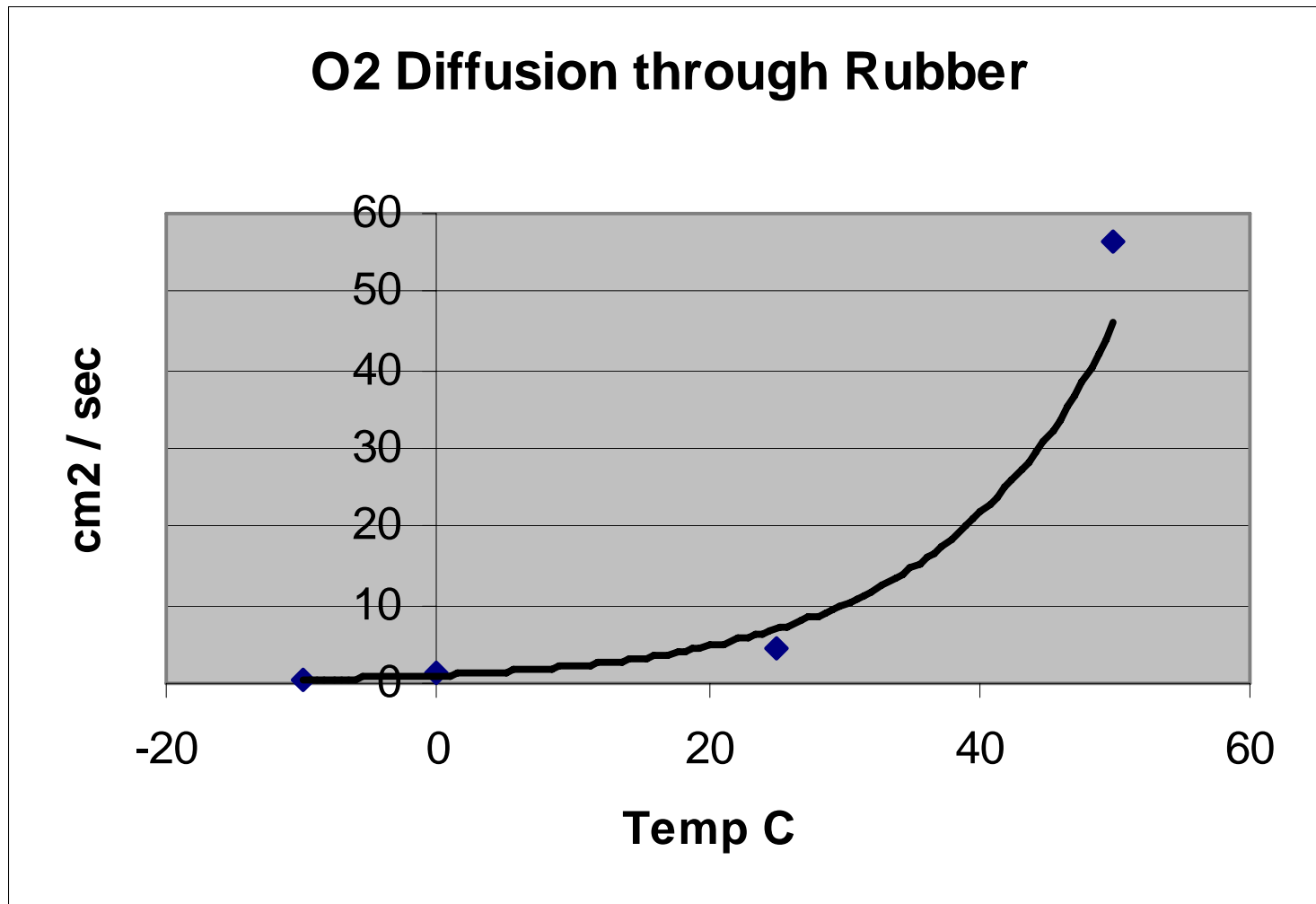
Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions.

Diffusion refers to the net transport of material within a single phase in the absence of mixing.

In Fickian systems, D is independent of concentration.

$$\text{Units of } D: \frac{cm^2}{sec}$$

Diffusion Coefficient vs. Temp



Solubility

Solubility represents the dissolution of permeant into polymer and relates the concentrations within the film to the partial pressure of the permeant.

Solubility is dependent upon permeant concentration or driving force.

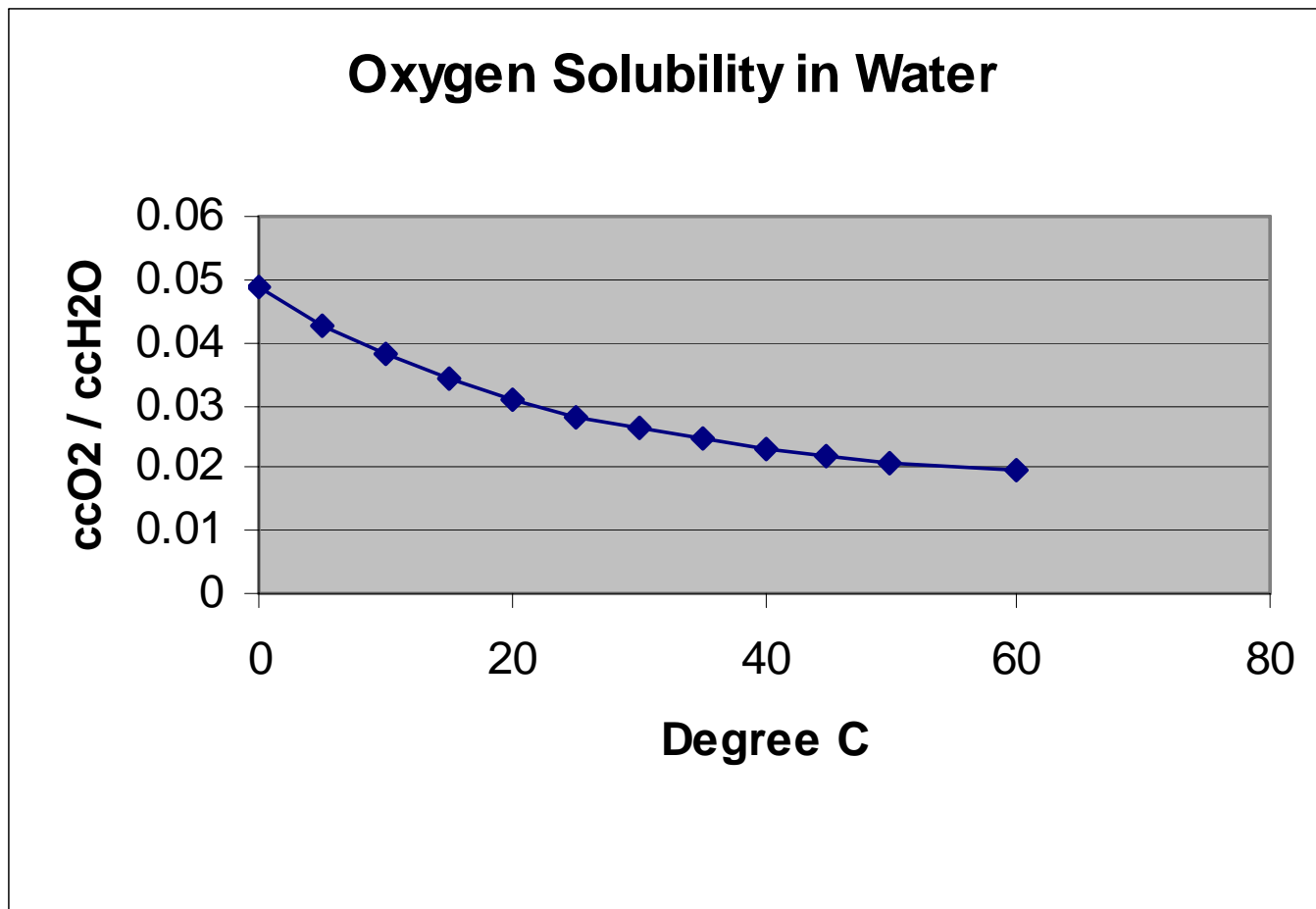
Units of S: $\frac{cm^3 (STP)}{cm^3 - mmHg}$

Real-life Solubility

- 2-liter bottle material used in a variety of food and beverage applications.
- At 23C with room air (20.9% oxygen) exposure, the bottle walls contained 0.48 cc's of oxygen



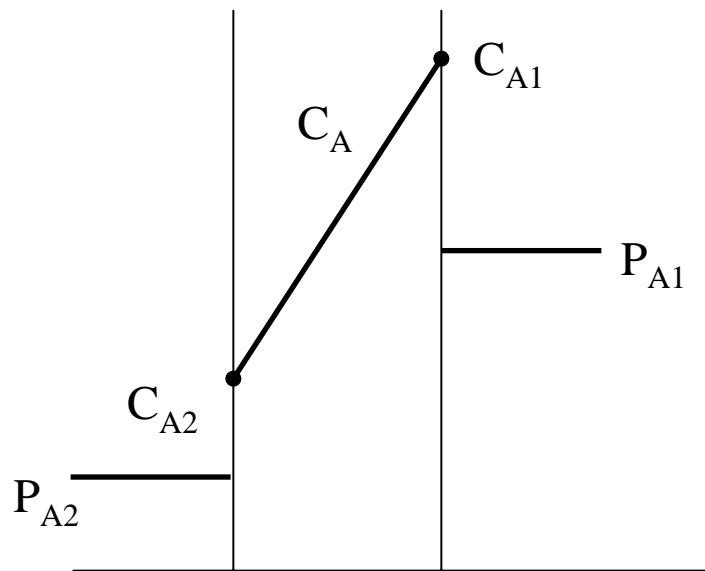
Solubility vs. Temperature



Temperature Impact on Permeation?

- As Temp Increases → Diffusion increases
- As Temp Increases → Solubility decreases
- $P = S \times D$
- D over-rides S in the above equation and....
- Generally: For every 10C increase in Temp, the Permeation Rate Doubles

Henry's Law



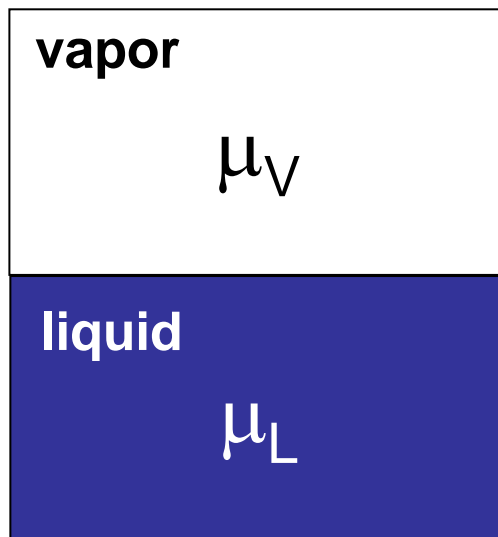
The concentrations are related to the partial pressures by a solubility coefficient, S (the reciprocal of Henry's Law coefficient)

$$C_A = P_A S_A$$

Chemical Potential

Chemical potential, μ , is the actual driving force for permeation.

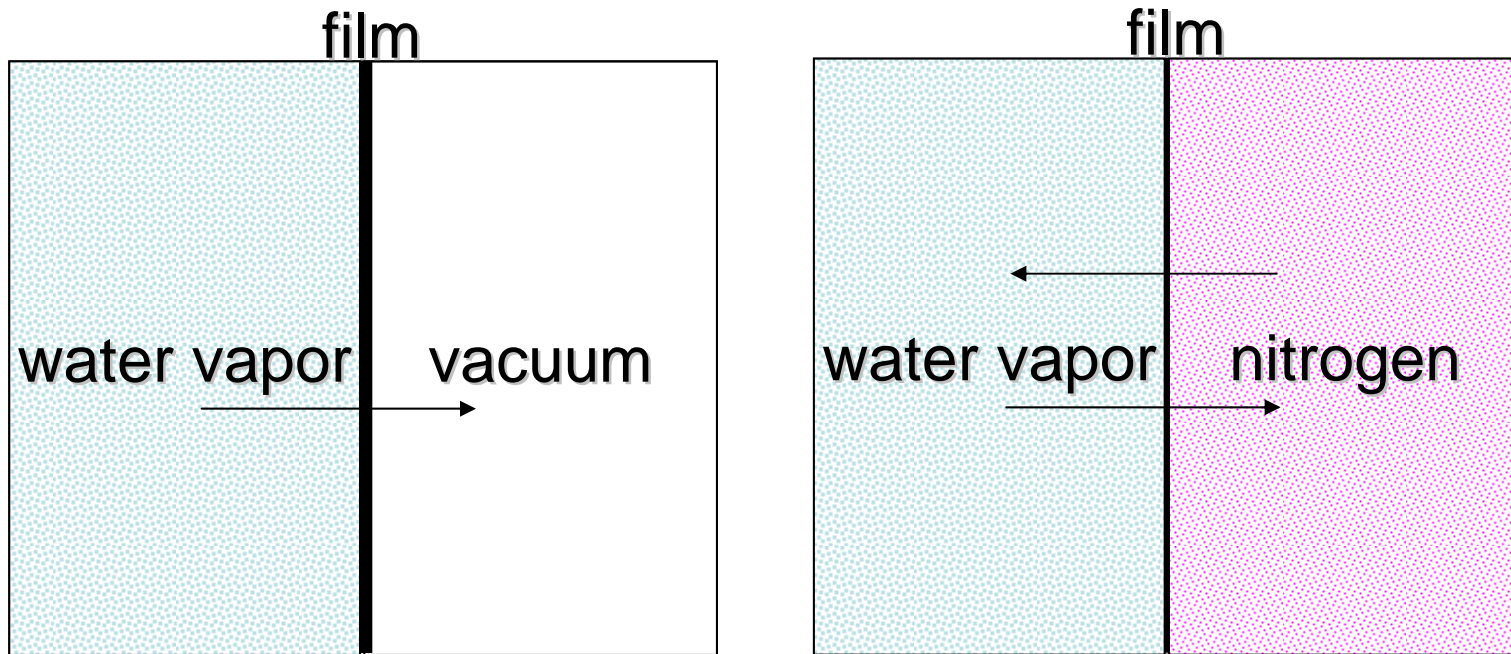
Chemical potential is a thermodynamic property related to pressure.



For *Vapor Liquid Equilibrium* (VLE),

$$\mu_L = \mu_V$$

Permeation



$$P_{wv} = x \quad \leftarrow \quad \begin{matrix} P_{wv} = x \\ P_{nitrogen} = y \end{matrix}$$

Temperature

Arrhenius equation:

$$P = P_0 e^{\frac{-E}{RT}}$$

P = Permeation rate

P_0 = Permeability constant

E = Activation energy

R = Gas constant

T = Temperature

Polymeric (MATERIAL) properties influencing package performance

- Structure
- Moisture and other possible interactants with the chains.
- Polymer surface
- Additives
- Thickness
- Multiple layers

Effect of the actual chemical substituent on the polymer backbone

- Polymer chains must “move aside” or “open up” to allow permeation.
- The weaker the forces holding the chains together, the more rapidly the permeation will occur.
- The chain-to-chain forces are determined by the chemical nature of the backbone.

Effect of the actual chemical substituent on the polymer backbone

POLYMER	STRUCTURE	OXYGEN PERMEATION*	COMMENTS
Polyethylene	$\text{H}_2\text{C}=\text{CH}_2$	480	Low polarity, very little cohesion between chains
Polypropylene	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{CH}_3 \end{array}$	150	Chains are a little stiffer, but very little cohesion or attraction
Poly(methyl methacrylate)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	17	Chains are much stiffer due to steric hindrances; polarity results in chain-to-chain attraction superior to hydrocarbon polymers
Poly(vinyl chloride)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$	8	Chain-to-chain attraction very high due to chlorine electrons; movement of chains restricted

* cc-mil/100 in²-day-atm

The degree of packing, crystallinity, and orientation of the molecular chains

- Close packing and/or high crystallinity results in low free volume and better barrier.
- Orientation results in better barrier by creating a more tortuous diffusion path.

POLYMER	MORPHOLOGY	O₂ PERMEATION*	COMMENTS
PET (poly(ethylene terephlate))	10% crystalline	10.0	
PET	50% crystalline	5.0	Higher crystallinity reduces the available sites for permeation
PET	50% crystalline and oriented	3.0	Crystallinity and orientation produces more tortuous path for permeation

* cc-mil/100 in²-day-atm

The susceptibility to moisture and other possible interactants with the chains

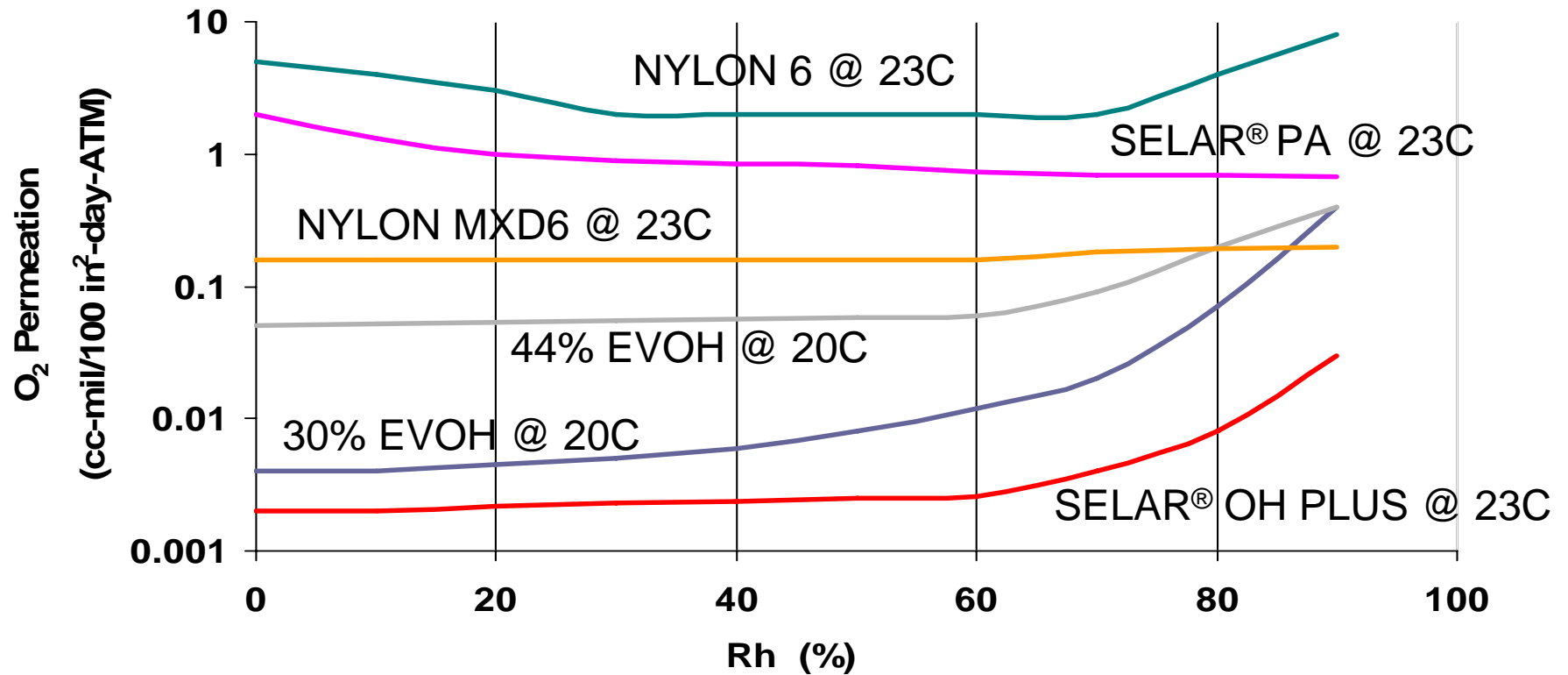
- **Some chemical species are adversely affected by moisture absorption and thus barrier is reduced.**
 - Water enters the polymer and interacts with the bonds that hold the chains together
 - The polymer swells and the chains become “floppy” thus allowing permeation to increase.
- **Water, which is highly polar, will only react this way with polar polymer groups that depend upon hydrogen bonds.**
 - Hydroxyl
 - Amide
- **Other polar groups, although they might absorb water, are not affected since their barrier properties do not depend upon hydrogen bonds.**
 - Ester
 - Cyano

Effect of Relative Humidity on OTR

(10^{11} mL*cm/cm²*sec*cmHg @25°C)

Polymer	0%RH	100%RH
PVOH	0.0006	1.5
Uncoated Cellophane	0.0078	12.0
Nylon 6	0.06	0.3
PVA	3.3	9.0
ABS	0.06	0.06
HDPE	6.6	6.6
LDPE	28.8	28.8

The susceptibility to moisture and other possible interactants with the chains



Note: Selar® PA is commercially available. SELAR® OH PLUS is currently out of commercial production. Data on 'OH PLUS' is for reference only. SELAR® is a registered trademark of E.I. du Pont de Nemours & Co.

The nature of the polymer surface contacting the permeant

- The nature of the surface can determine the permeability as much as the polymer bulk.
- An example is hydrocarbon permeation through polyethylene:
 - Polyethylene polymer is very nonpolar and thus a very poor barrier to nonpolar permeants such as hydrocarbon liquids.
 - By treating the surface with fluorine gas, the fluorine adds on to the chains at or near the surface and by virtue of its bulk and polarity prevents hydrocarbon liquids from entering the polymer

Additives used in manufacturing or modifying the polymer

- Depending upon the chemical nature, as well as the manner which the additive is blended, the barrier can be either enhanced or reduced.

PVC		
Poly (vinyl chloride)		
Material state	Pure, rigid PVC	Plasticized, soft PVC
O₂ Permeation rate (cc-mil/100 in²-day-atm)	8	150

Presence of Co-permeant

Example – ethyl acetate and limonene, used with BOPP

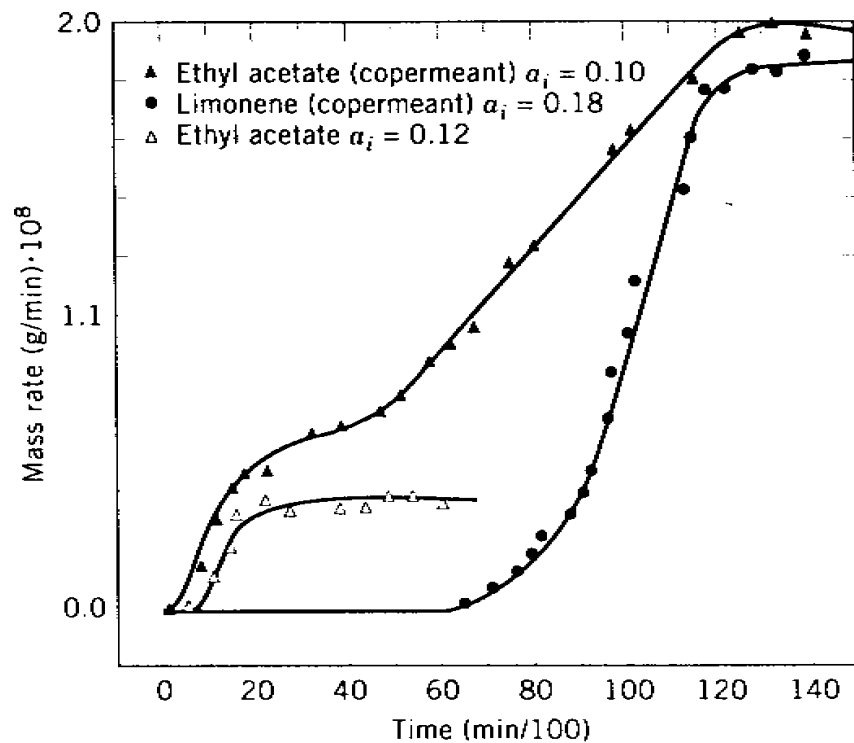


Figure 4. Comparison of the transmission profile of the binary mixture, ethyl acetate $\alpha_i = 0.1$ /limonene $\alpha_i = 0.18$, with the transmission profile of ethyl acetate ($\alpha_i = 0.12$) through oriented polypropylene.

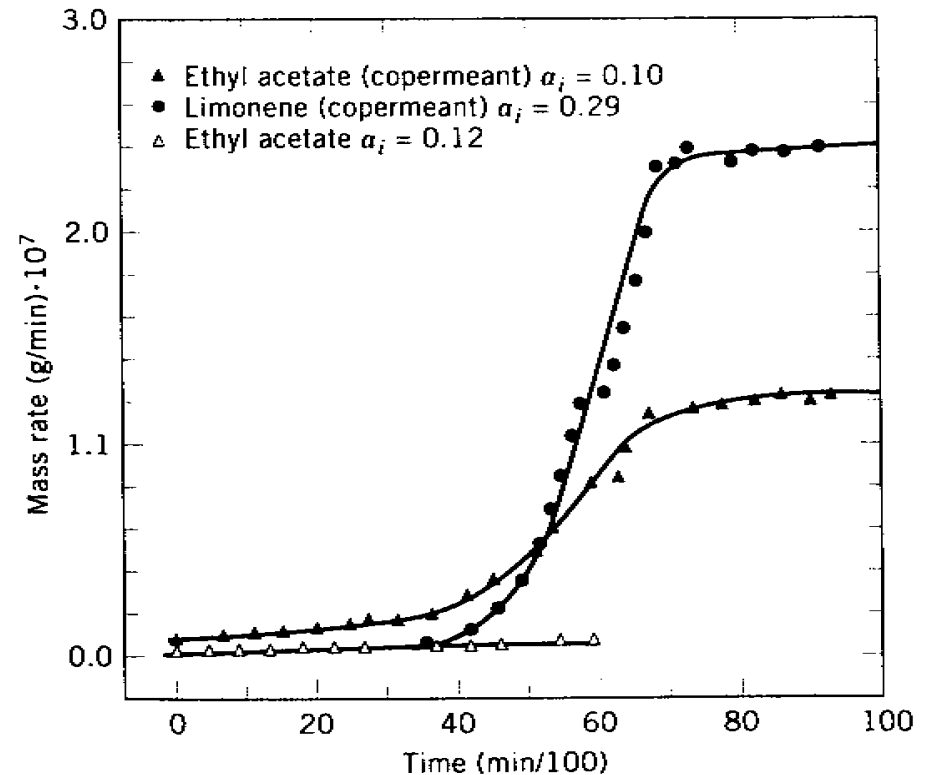


Figure 5. Comparison of the transmission profile of the binary mixture, ethyl acetate $\alpha_i = 0.1$ /limonene $\alpha_i = 0.29$, with the transmission profile of ethyl acetate ($\alpha_i = 0.12$).

Thickness

- Typically the transmission rate is inversely proportional to the thickness of the material

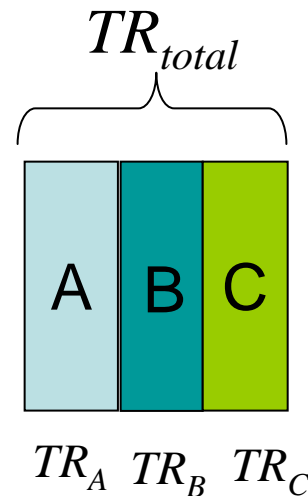
thickness ↑ permeation rate ↓

- This may not apply for very thin materials where structural changes or surface phenomena may have occurred.

Multiple layers

- Multi-layer materials obeying Fick's can be mathematically “added” by means of the *Parallel Resistance Equation*.

$$\frac{1}{TR_{total}} = \frac{1}{TR_A} + \frac{1}{TR_B} + \dots$$



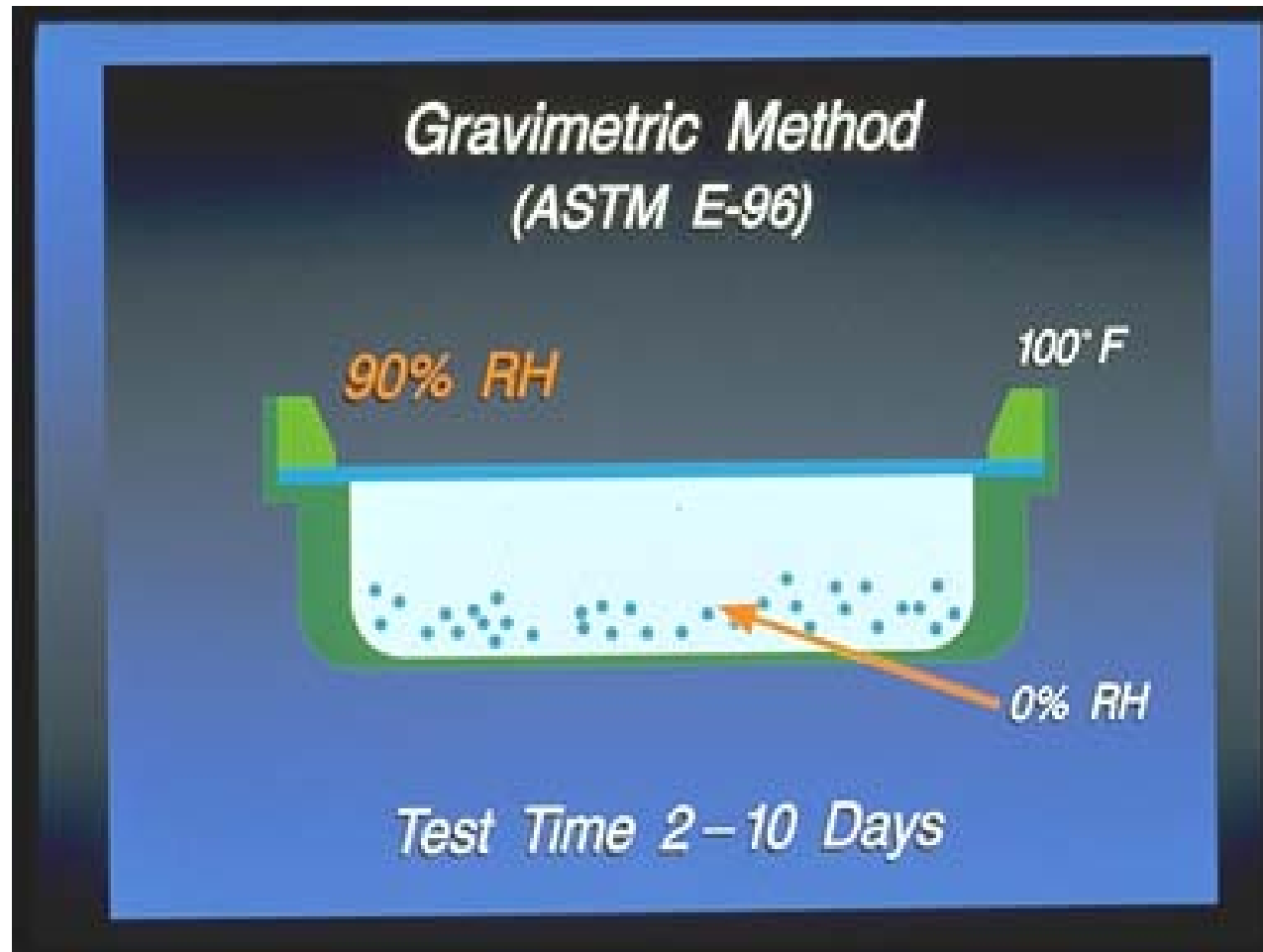
Measurement Techniques

Basic test methods for measuring permeation

- Gravimetric
- Isostatic
 - Flow-through
 - Accumulation / Speciation
- Accumulation //

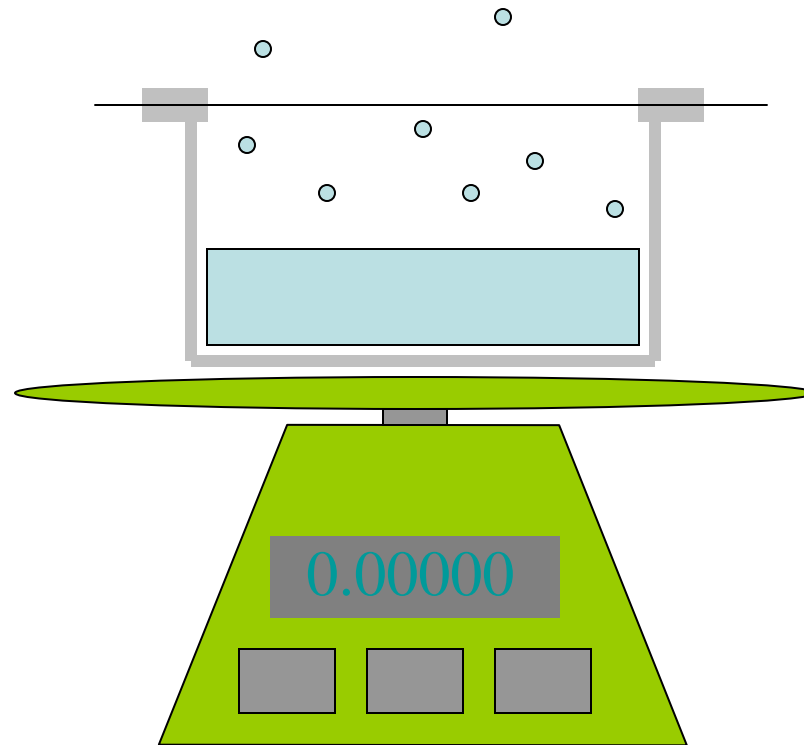
Gravimetric method

(dry cup - weight gain)



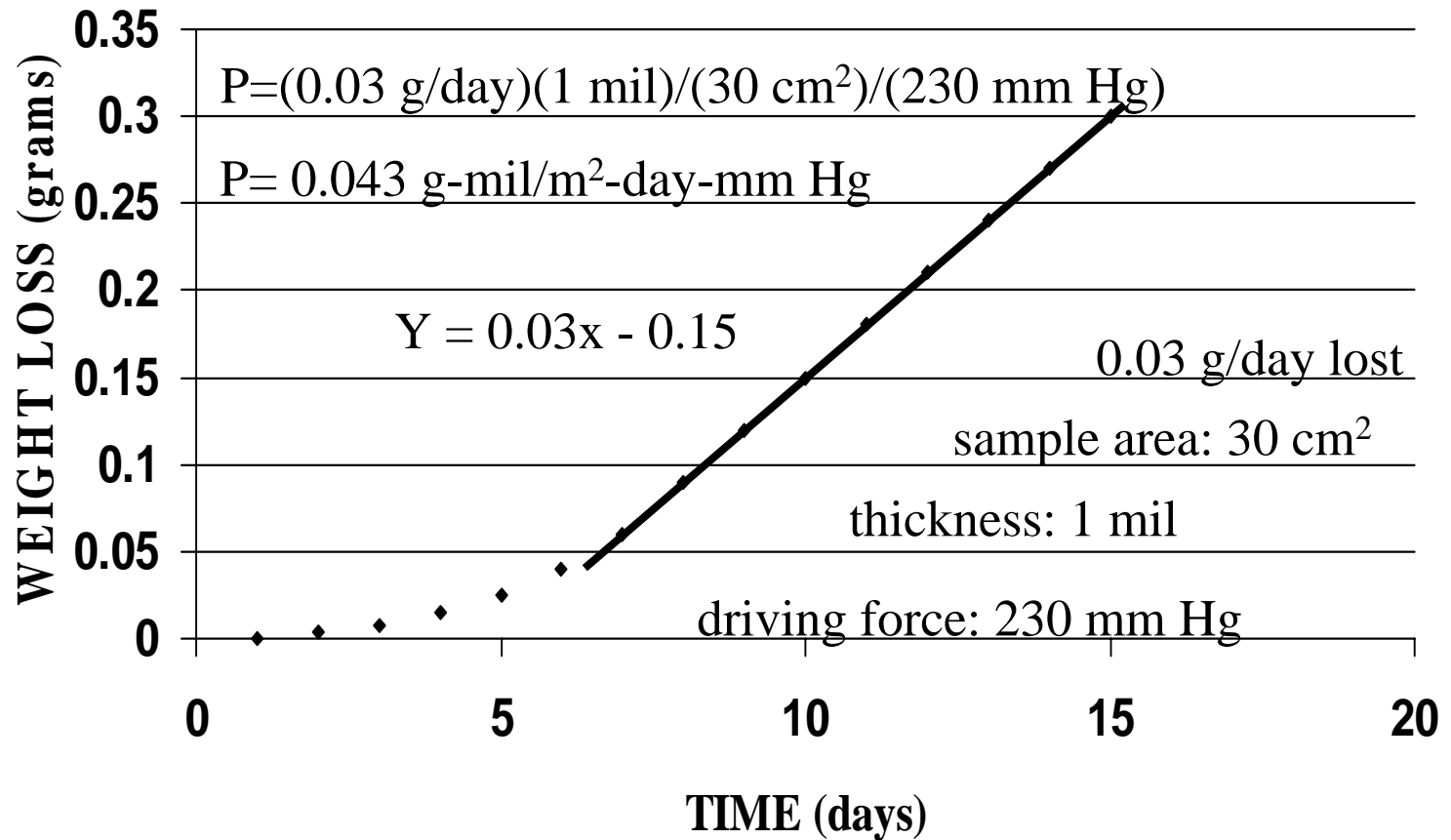
Gravimetric method

(wet cup - weight loss)



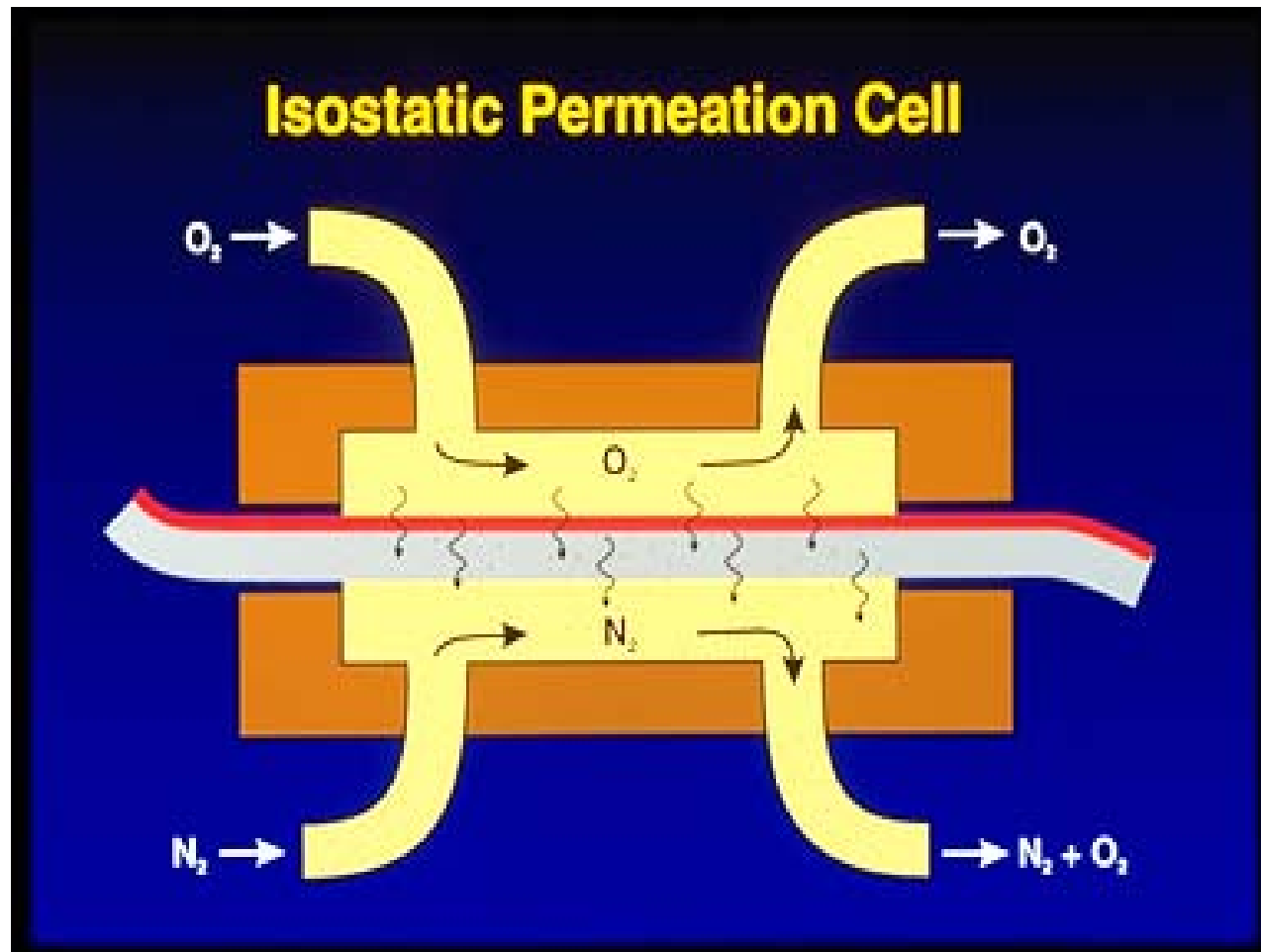
Gravimetric method

Data collection



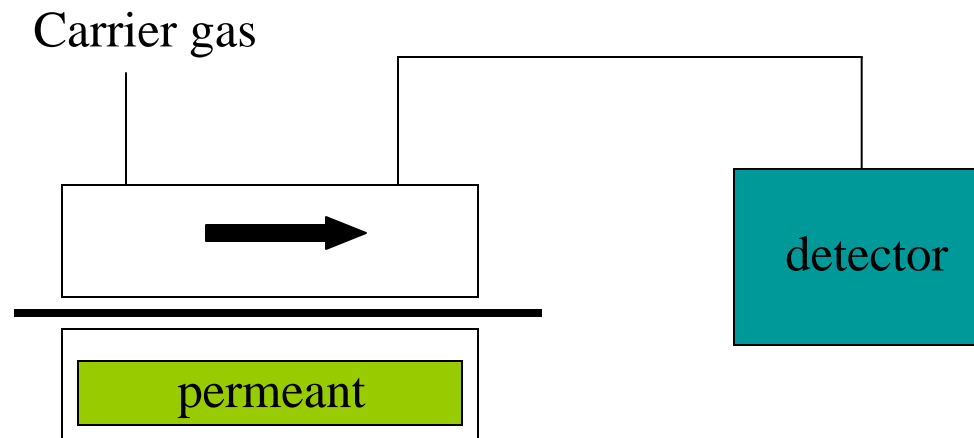
Isostatic Permeation Measurement

Flow-through technique



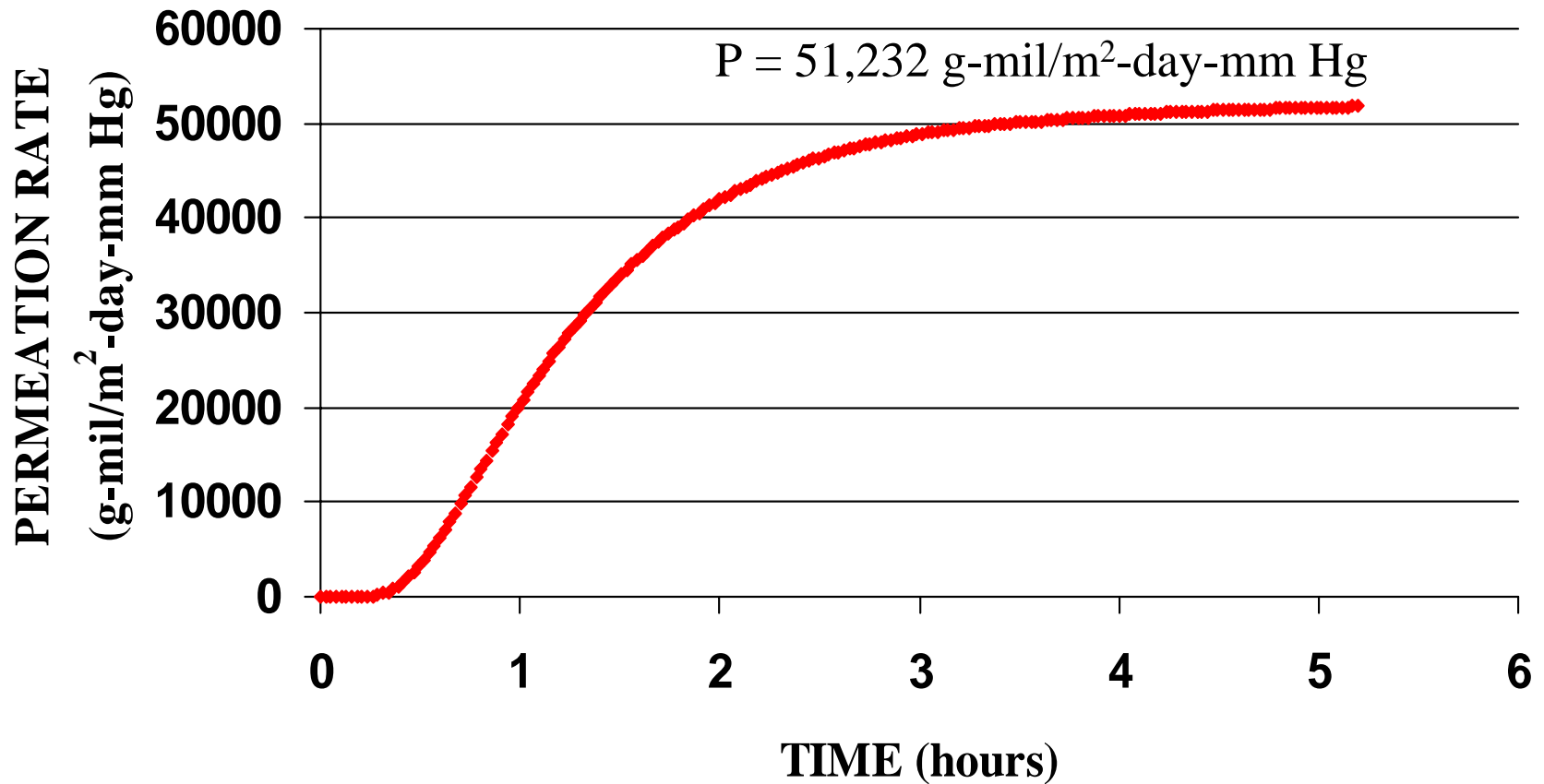
Isostatic Permeation Measurement

Flow-through technique



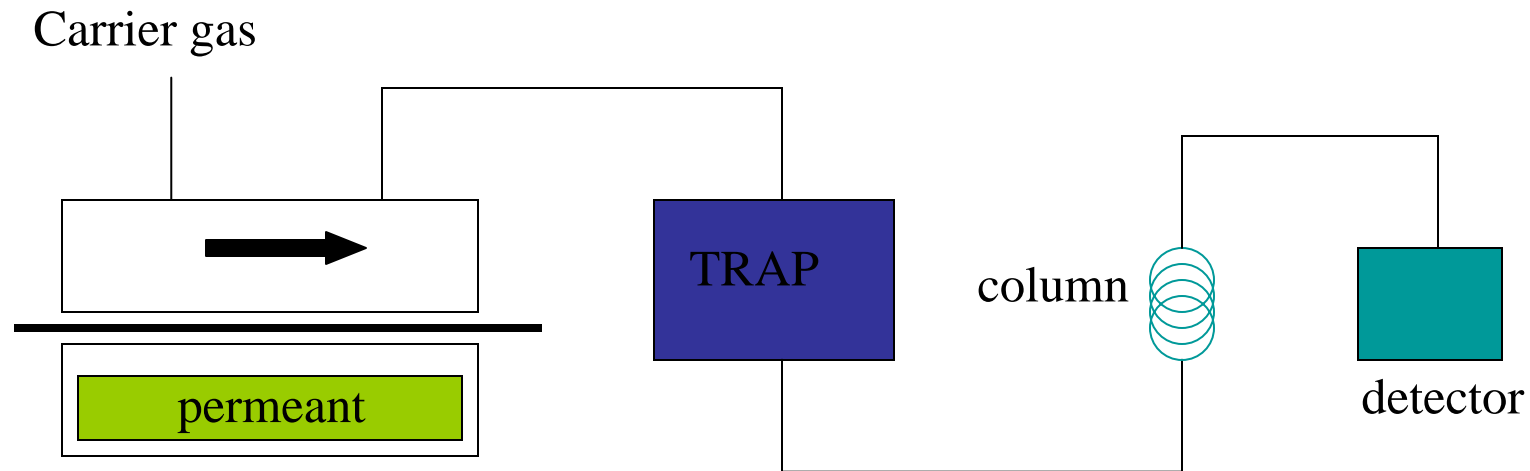
Isostatic Permeation Measurement

Data collection



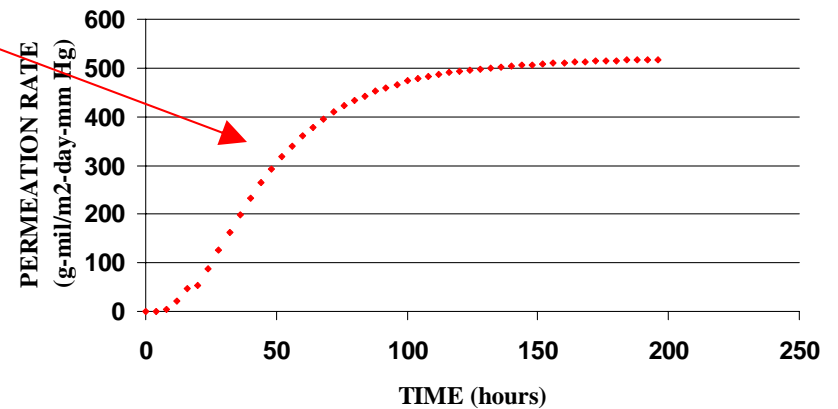
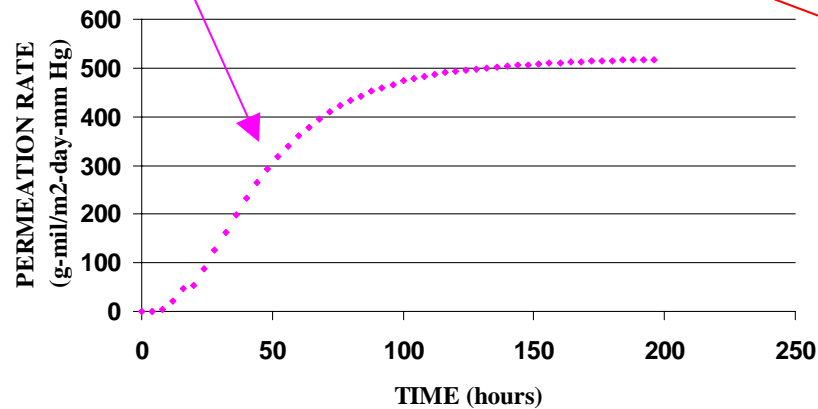
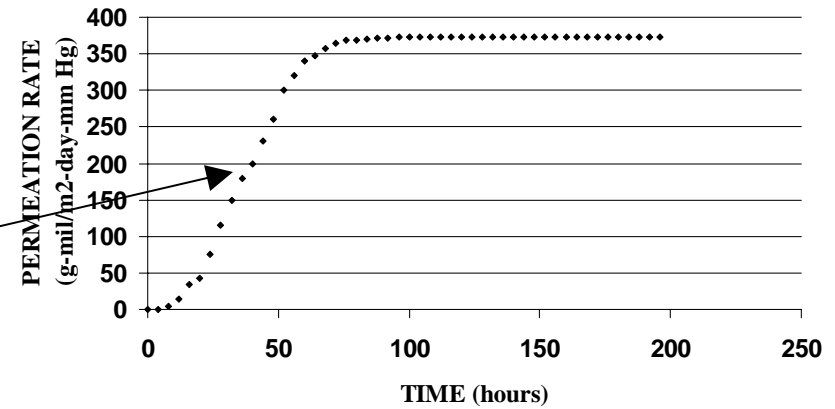
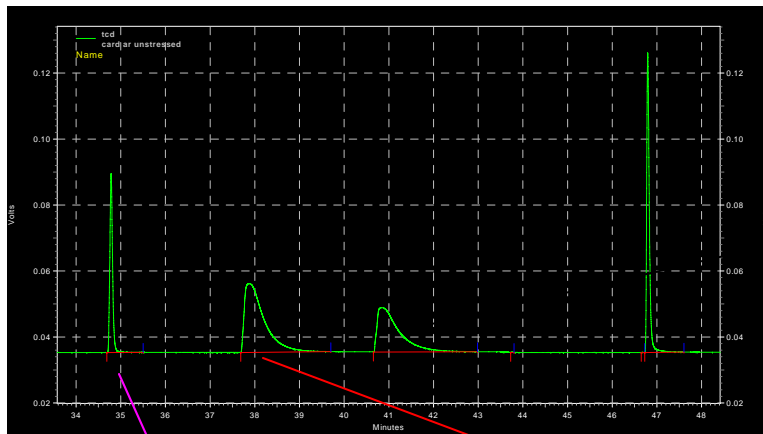
Isostatic Permeation Measurement

Accumulation / separation technique

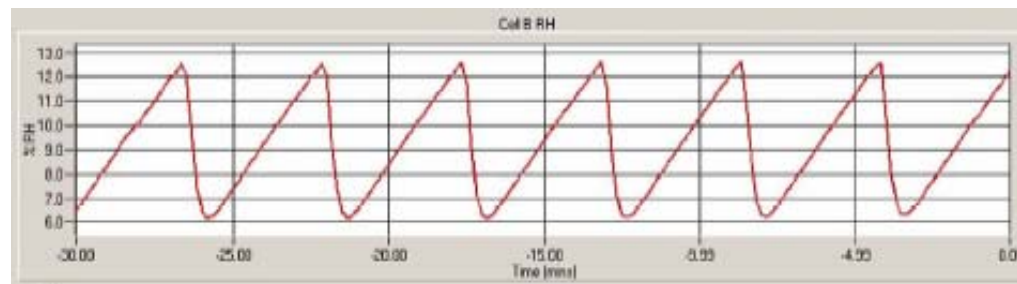
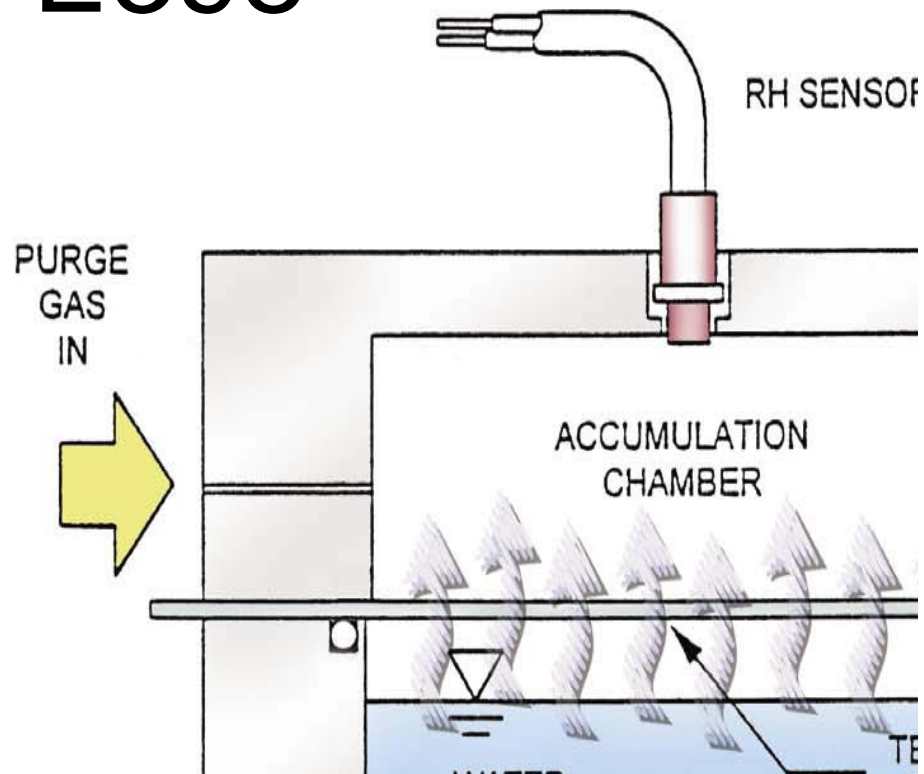


Isostatic Permeation Measurement

Data collection



Accumulation // ASTM E398



QUESTIONS??

Thank You

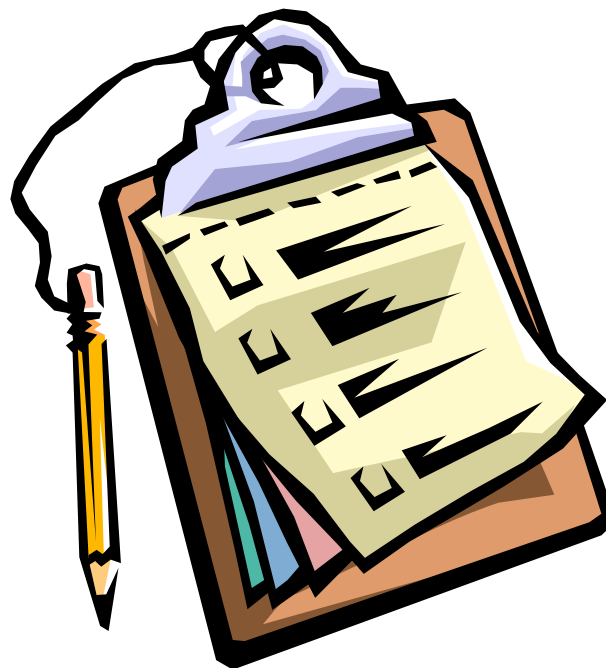
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*Please remember to turn
in your evaluation sheet...*