1.1 Multilayer materials

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Compact formula are obtained by noting with an index $j=0$ the food product and $j=1..n$ the n plastic layers of the packaging material. The layer 1 is the layer in contact with food as described in figure 1. The thickness of each layer is noted l_j. By convention, l_0 is related to the half thickness of the food product since the product is assumed to be symmetrically in contact with the same material. If it is not the case (e.g. film sheet on a single side), l_0 must be replaced by the whole thickness.
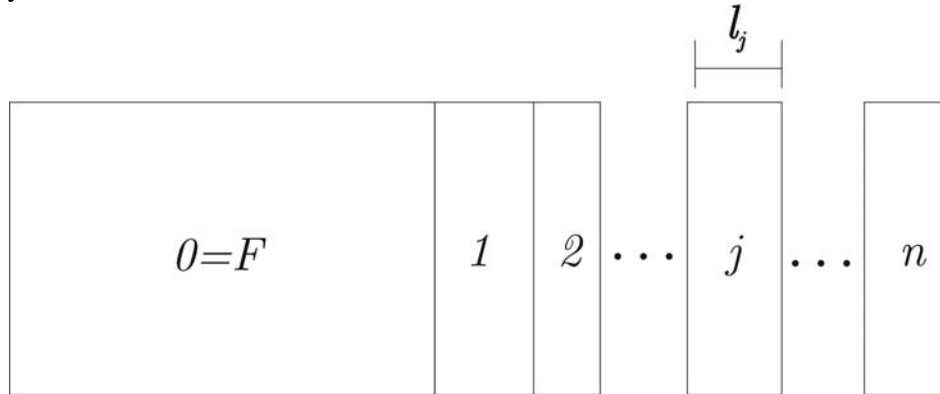

Figure 1. Indexing of n-multilayers materials in contact with food.

1.1.1 Thermodynamic equilibrium

1.1.1.1 *Sorption and desorption properties*

The equilibrium of sorption and sorption in each layer is assumed to be reversible and obey to Henry law. As a result, an equivalent vapor pressure of the substance in equilibrium with the amount of the substance dispersed locally in each layer j is defined as follow:

$$\underbrace{p_j(x)}_{\text{Pa}} = \underbrace{k_j}_{\frac{k_j^H \cdot \rho_j}{M}} \cdot \underbrace{C_j(x)}_{\text{kg·kg}_j^{-1}} \tag{1}$$

where k_j^H and ρ_j are respectively the Henry coefficient of the substance in the layer j and ρ_j the density of the layer j. M is the molecular mass of the considered substance. It is worth to notice that k_j^H (with units in J·mol^{-1}) is also the reciprocal of the solubility of the substance in the layer j.

1.1.1.2 *Condition of equilibrium between j_1 and j_2*

Two layers, noted j_1 and j_2, at a same temperature without external mechanical constraints (*i.e.* at the same pressure) are at thermodynamical equilibrium when their activity and consequently their partial pressures in desorbable substances are equal:

$$p_{j_1}\big|_{eq} = p_{j_2}\big|_{eq} \Leftrightarrow K_{j_1/j_2} = \frac{C_{j_1}\big|_{eq}}{C_{j_2}\big|_{eq}} = \frac{k_{j_2}}{k_{j_1}} \tag{2}$$

where K_{j_1/j_2} is the partition coefficient of the considered substance between j_1 and j_2. $C_{j_1}\big|_{eq}$ and $C_{j_2}\big|_{eq}$ are the concentrations at equilibrium respectively in layers j_1 and j_2.

1.1.1.3 *Mass balance considerations*

By assuming that the considered substance is initially only present in the packaging material and not in the food product, the mass balance between the food product and the packaging material is written:

$$\sum_{j=1}^{n}\left(\rho_j \cdot \underbrace{C_j\big|_{eq}}_{k_0/k_j \cdot C_0|_{eq}} \cdot l_j\right) + \rho_0 C_0\big|_{eq} \cdot l_0 = \sum_{j=1}^{n}\left(\rho_j \cdot C_j\big|_{t=0} \cdot l_j\right) \tag{3}$$

By noticing that the condition of equilibrium enforces $\left\{p_j\big|_{eq}\right\}_{j=1..n} = p_0\big|_{eq}$, the concentration in food at equilibrium is finally given by:

$$C_0\big|_{eq} = \frac{\displaystyle\sum_{j=1}^{n}\left(\frac{\rho_j}{\rho_0}\cdot\frac{l_j}{l_0}\cdot C_j\big|_{t=0}\right)}{1+\displaystyle\sum_{j=1}^{n}\left(\frac{k_0}{k_j}\cdot\frac{\rho_j}{\rho_0}\cdot\frac{l_j}{l_0}\right)} \tag{4}$$

The corresponding partial pressure at equilibrium is equivalently as a function of the initial partial pressure in each layer:

$$p_0\big|_{eq} = \left\{p_j\big|_{eq}\right\}_{j=1..n} = \frac{\displaystyle\sum_{j=1}^{n}\left(\frac{k_0}{k_j}\cdot\frac{\rho_j}{\rho_0}\cdot\frac{l_j}{l_0}\cdot p_j\big|_{t=0}\right)}{1+\displaystyle\sum_{j=1}^{n}\left(\frac{k_0}{k_j}\cdot\frac{\rho_j}{\rho_0}\cdot\frac{l_j}{l_0}\right)} \tag{5}$$

Equations (4) and (5) generalize the equation (??) to multilayer materials. It is worth to notice that they do not require that the layers are initially at equilibrium. However, they assume that the initial concentration is uniform in each layer. When it is not the case, equation (4) must be replaced by a continuous integration over each layer. For general 1D geometries, one gets:

$$C_0\big|_{eq} = \frac{\displaystyle\sum_{j=1}^{n}\left(\frac{1}{\rho_0}\cdot\int_{l_{j-1}^c}^{l_j^c}\rho_j\cdot C_j\big|_{t=0}^{(x)}\cdot x^m\cdot dx\right)}{\displaystyle\int_0^{l_0}x^m\cdot dx + \frac{1}{\rho_0}\cdot\sum_{j=1}^{n}\left(\int_{l_{j-1}^c}^{l_j^c}\frac{k_0}{k_j}\cdot\rho_j\cdot x^m\cdot dx\right)} \tag{6}$$

Where $m=0,1,2$ respectively for Cartesian, cylindrical and spherical coordinates. $l_j^c = \sum_{j=0}^{n}l_j$ is the cumulated thickness (starting from the product).

For convenience and according to equation (2), choosing $k_0=1$ leads to identify k_j to the partition coefficient between the food product and the packaging layer j.

1.1.2 Transport equations

By assuming a local thermodynamical equilibrium at the interfaces between all layers (including the food product), the partial pressure is continuous over all layers. As a result, the partial pressure seems a best choice to implement transport equations in commercial numerical codes. This choice leads to express the local mass flux in the layer j as a consequence of a gradient in partial pressure:

$$\underset{kg \cdot m^{-2} \cdot s^{-1}}{\underbrace{J_j}} = -\underset{m^2 \cdot s^{-1}}{\underbrace{D_j}} \cdot \underset{kg \cdot m^{-3}}{\underbrace{\rho_j}} \cdot \frac{\partial C_j}{\partial x} = -\frac{D_j \cdot \rho_j}{k_j} \cdot \frac{\partial p_j}{\partial x} = -\alpha_j \cdot \frac{\partial p_j}{\partial x} \tag{7}$$

If the D_j can be considered uniform in the layer $j>1$, $\alpha_j = \dfrac{D_j \cdot \rho_j}{k_j} = D_j \cdot \delta_j$ is a new equivalent transport property. The equivalent local mass balance is accordingly written for any layer j as:

$$\delta_j \cdot \frac{\partial p_j}{\partial t} = \frac{1}{x^m} \frac{\partial}{\partial x}\left(x^m \cdot \alpha_j \cdot \frac{\partial p_j}{\partial x} \right) \quad \text{for } j=1..n \tag{8}$$

Since significant discrepancies may be expected between $\{\alpha_j\}_{j=1..n}$ values and between $\{\delta_j\}_{j=1..n}$ values, a dimensionless formulation seems preferable to preserve the numerical stability of the discretization scheme.

By analogy with permeation, the reference length scale, l_{ref}, is associated to the layer with the maximum mass transfer resistance (noted j_{ref}), that is with the lowest $\{\alpha_j/l_j\}_{j=1..n}$ value. The dimensionless time or Fourier number, Fo, is expressed as:

$$Fo = \frac{\alpha_{j_{ref}} \cdot t}{l_{ref}^2} \tag{9}$$

An almost dimensionless formulation is finally obtained:

$$\delta_j \cdot \frac{\partial p_j^*}{\partial Fo} = \frac{1}{x^{*m}} \frac{\partial}{\partial x^*}\left(x^{*m} \cdot \frac{\alpha_j}{\alpha_{j_{ref}}} \cdot \frac{\partial p_j^*}{\partial x^*} \right) \quad \text{for } j=1..n \tag{10}$$

with $x^* = \dfrac{x}{l_{ref}}$ and $p_j^* = \dfrac{p_j}{p_0|_{eq}}$.

At the interface between $j=1$ and $j=0$, that is at the position $x=0$, the boundary condition is written:

$$J|_{x=0} = -\alpha_1 \cdot \left.\frac{\partial p_1}{\partial x}\right|_{x=0} = h \cdot \left(\frac{\rho_0}{k_0} \cdot p_1|_{x=0} - \frac{1}{l_0} \cdot \int_0^t J|_{x=0} \cdot d\tau \right) \tag{11}$$

By introducing the dimensionless flux $J^*|_{x=0} = -\dfrac{\alpha_1}{\alpha_{ref}} \cdot \left.\dfrac{\partial p_1^*}{\partial x^*}\right|_{x^*=0} = \dfrac{1}{p_0|_{eq}} \cdot \dfrac{l_{ref}}{\alpha_{ref}} \cdot J|_{x=0}$, one gets the dimensionless boundary condition:

$$J^*|_{x=0} = Bi \cdot \left(\frac{p_1^*|_{x=0}}{k_0} - L \cdot \int_0^{Fo} J^*|_{x=0} \cdot d\tau \right) \tag{12}$$

where $Bi = \dfrac{h \cdot \alpha_{ref}}{l_{ref}}$ is the mass Biot number and $L = \dfrac{l_{ref}}{l_0}$ is associated to a dilution factor.

An impervious boundary condition is assumed at $x^* = 1$:

$$\left.\frac{\partial p_1^*}{\partial x^*}\right|_{x=1} = 0 \tag{13}$$