Module : 5
Gas separation

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Gas Separation

In case of gas separation by membranes, high pressure feed gas is supplied to one side of the membrane and permeate comes out normal to the membrane to the low pressure side. Due of high diffusivity in gases, concentration gradient in the gas phase normal to the membrane surface is small. So, gas film resistance is neglected compared to membrane resistance. This means concentration in gas phase in a direction normal to membrane is uniform whether gas stream flows parallel to the surface or not.

There are various types of gas separation processes depending upon the flow characterizations. Since the permeate comes normal to the flow direction of the feed, this is known as simple cross flow (Fig. 5.1a). If there is complete mixing of the feed and permeate by an external agent (stirrer or mixer), then the configuration is complete mixing (Fig. 5.1b). If feed and permeate are in the same direction, then the flow is cocurrent flow (Fig. 5.1c). If they are in opposite direction, then it is counter current flow (Fig. 5.1d).

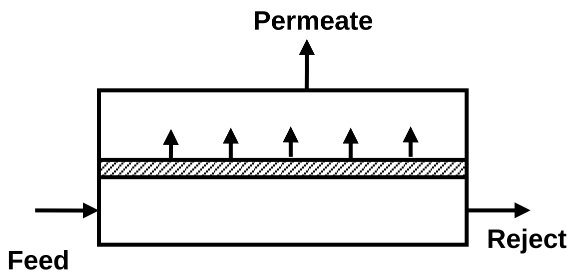


Fig. 5.1a: Cross Flow

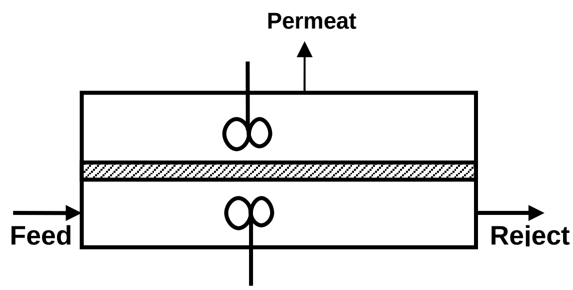


Fig. 5.1b: Complete Mixing

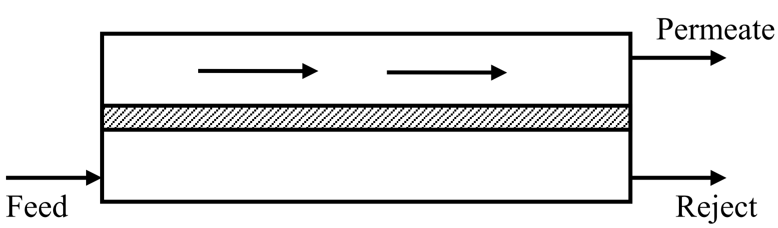


Fig. 5.1c:Co-current

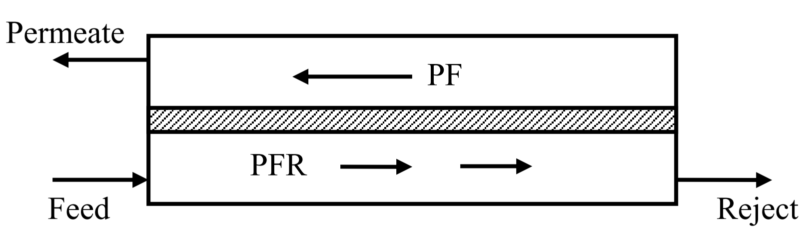


Fig. 5.1d: Counter current

In the following section, the working principles and calculations involved in complete mixing mode are considered. This case is like a continuous stirred tank reactor (CSTR). The assumptions involved are:

(i) Isothermal condition.

(ii) Negligible pressure drop in feed and permeate side.

(iii) Permeability of each component is constant.

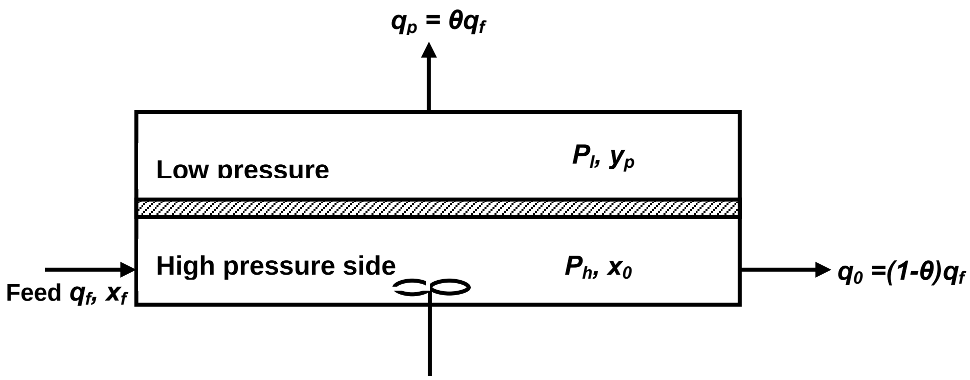


Fig. 5.2: Schematic of a complete mixing configuration with the process conditions

In the above figure, q_f is total feed flow rate (in m^3/s) ; q_0 is outlet reject flow (m^3/s) ; q_p is outlet permeate flow (m^3/s) ; θ *is* fraction of feed permeate $= \dfrac{q_p}{q_f}$.

Overall material balance yields the following relation.

$$q_f = q_0 + q_p \tag{5.1}$$

Rate of diffusion/ permeation of species A (in a binary mixture of A and B) is given as,

$$\frac{q_A}{A_m} = \frac{q_p y_p}{A_m} = \left(\frac{P_A'}{t}\right)\left(P_h x_0 - P_l y_p\right) \tag{5.2}$$

where, $P_A^{'}$ is permeability of A in membrane $\left(\frac{cm^3.cm}{s.cm^2.cmHg}\right)$; q_A is the flow rate of A in permeate; A_m is the membrane area; t is the membrane thickness; P_h is feed side total pressure ($cm.Hg$); x_0 is mole fraction of A in reject; x_f is mole fraction of A in feed; y_p is mole fraction of A in permeate; $P_h x_0$ is partial pressure of A in reject gas phase. Rate of permeation of species B is given as,

$$\frac{q_B}{A_m} = \frac{q_p\left(1-y_p\right)}{A_m} = \frac{P_B^{'}}{t}\left[P_h\left(1-x_0\right)-P_l\left(1-y_p\right)\right] \tag{5.3}$$

Where, $P_B^{'}$ is permeability of B. Dividing Eq.(5.2) by (5.3), the following expression is obtained.

$$\frac{y_p}{1-y_p} = \frac{\alpha^*\left[x_0-\left(\frac{P_l}{P_h}\right)y_p\right]}{\left(1-x_0\right)-\left(\frac{P_l}{P_h}\right)\left(1-y_p\right)} \tag{5.4}$$

Where, $\alpha^* = \frac{P_A^{'}}{P_B^{'}}$

Overall component balance for A:

An overall balance of component A results into the following equation.

$$q_f x_f = q_0 x_0 + q_p y_p \tag{5.5}$$

Rearrangement of above equation results,

$$x_f = \frac{q_0 x_0}{q_f} + \frac{q_p y_p}{q_f} \tag{5.6}$$

Defining, $\frac{q_p}{q_f} = \theta$; and $\frac{q_0}{q_f} = 1-\theta$, the above equation is written as,

$$x_f = (1-\theta)x_0 + \theta y_p \tag{5.7}$$

The above equation is re-organized to estimate the feed mole fraction or that in the permeate.

$$x_0 = \frac{x_f - \theta y_p}{1-\theta} \quad \text{or} \quad y_p = \frac{x_f - x_0(1-\theta)}{\theta} \tag{5.8}$$

But, $q_p = \theta q_f$ and the membrane area can be estimated as follows.

$$\frac{q_p y_p}{A_m} = \left(\frac{P_A^{'}}{t}\right)\left(P_h x_0 - P_l y_p\right)$$

$$A_m = \frac{\theta q_f y_p}{\left(\frac{P_A^{'}}{t}\right)\left(P_h x_0 - P_l y_p\right)} \tag{5.9}$$

For design purposes:

There are 7 variables, namely, $x_f, x_0, y_p, \theta, \alpha^*, \frac{P_l}{P_h}, A_m$. 4 of them are generally independent.

<u>Case 1:</u> $x_f, x_0, \alpha^*, \frac{P_l}{P_h}$ are given and y_p, θ, A_m need to be determined.

From Eq. (5.3),

$$y_p = y_p\left(x_0, \alpha^*, \frac{P_l}{P_h}\right) \tag{5.10}$$

It is a quadratic equation. We can solve for y_p. θ is calculated from Eq. (5.8)

$$x_0 = \frac{x_f - \theta y_p}{1-\theta}$$

A_m can be calculated from Eq. (5.9).

Case 2: $x_f, \theta, \alpha^*, \frac{P_l}{P_h}$ are given and y_p, x_0, A_m to be calculated

Minimum concentration of Reject Stream:

If all the feed is permeated, then θ=1 and feed composition $x_f = y_p$

For all values of θ <1, $y_p > x_f$

Substitute, $x_f = y_p$ in Eq. (5.3).

x_{0m} = Minimum rejection component for a given x_f

$$= \frac{x_f\left[1+\left(\alpha^*-1\right)\left(\frac{P_l}{P_h}\right)\left(1-x_f\right)\right]}{\alpha^*\left(1-x_f\right)+x_f} \tag{5.11}$$

So, a feed component x_f cannot be stripped lower than x_{0m} even with an infinitely large membrane area for a completely mixed system. To do this cascade may be used.

Cross Flow model for gas Permeation:

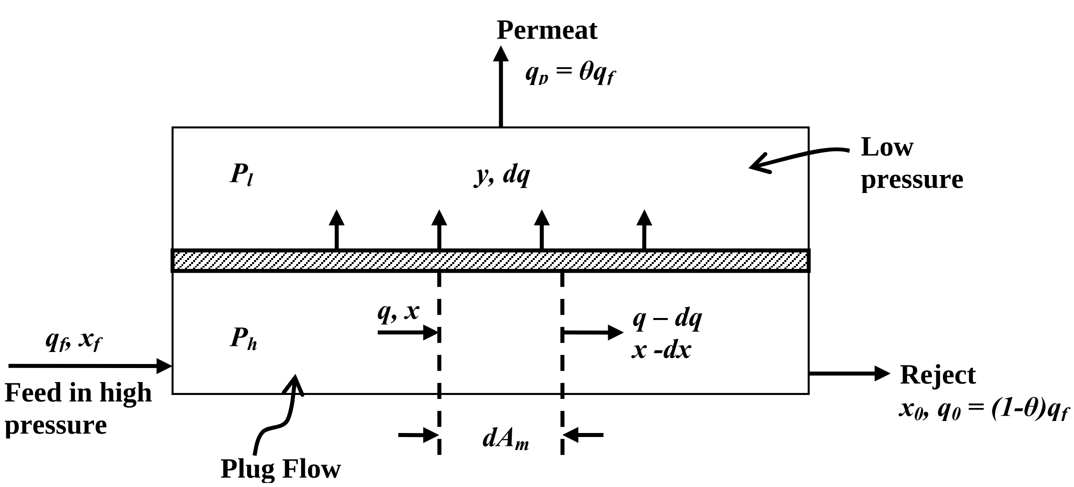


Fig. 5.3: Schematic of a cross flow model

Longitudinal velocity in high pressure or reject stream is high. So that gas is in plug flow and flows parallel to membrane. Low pressure side, permeate stream is almost pulled into vacuum. So, flow is essentially perpendicular to membrane. No mixing is assumed. So that composition varies as length. Over a different membrane area dA_m at any point, local permeation rates are presented below.

Component A balance:

$$-ydq = \frac{P_A^{'}}{t}\left[P_h x - P_l y\right] dA_m \tag{5.12}$$

Component B balance:

$$-(1-y)\,dq = \frac{P_B^{'}}{t}\left[P_h(1-x) - P_l(1-y)\right] dA_m \tag{5.13}$$

dq = total flow rate perpendicular to dA_m. Dividing Eq.(5.12) by (5.13),

$$\frac{y}{1-y} = \frac{\alpha^{*}\left[x - \left(\dfrac{P_l}{P_h}\right)y\right]}{(1-x) - \left(\dfrac{P_l}{P_h}\right)(1-y)} \tag{5.14}$$

Permeate composition y as a function of reject composition x at a point along the length.

Analytical solution:

The design equation is presented below:

$$\frac{(1-\theta^{*})(1-x)}{(1-x_f)} = \left(\frac{u_f - \dfrac{E}{D}}{u - \dfrac{E}{D}}\right)^{R} \left(\frac{u_f - \alpha^{*} + F}{u - \alpha^{*} + F}\right)^{S} \left(\frac{u_f - F}{u - F}\right)^{T} \tag{5.15}$$

Where, $\theta^{*} = 1 - \dfrac{q}{q_f}$, $i = \dfrac{x}{1-x}$; $u = -Di + \sqrt{D^2 i^2 + 2Ei + F^2}$;

$$D = 0.5\left[\frac{\left(1-\alpha^*\right)P_l}{P_h} + \alpha^*\right]; \qquad E = \frac{\alpha^*}{2} - DF; \qquad F = -0.5\left[\left(1-\alpha^*\right)\frac{P_l}{P_h} - 1\right]$$

$$R = \frac{1}{2D-1}; \qquad S = \frac{\alpha^*\left(D-1\right)+F}{\left(2D-1\right)\left(\frac{\alpha^*}{2}-F\right)}; \qquad T = \frac{1}{1-D-\frac{E}{F}}$$

u_f=value of u at $i = i_f = \dfrac{x_f}{1-x_f}$.

Composition of exit:

At exit, $x=x_0$, $\theta^* = \theta$ (cut ratio) = fraction of feed permeated.

y_p= mole fraction at the exit of permeate is estimated by overall material balance

Membrane area required,

$$A_m = \frac{tq_f}{P_h P_B'}\int_{i_0}^{i_f} \frac{\left(1-\theta^*\right)\left(1-x\right)}{\left(f_i - i\right)\left[\frac{1}{1+i} - \frac{P_l}{P_h}\left(\frac{1}{1+f_i}\right)\right]} di \qquad (5.16)$$

Where, $f_i = \left(D_i - F\right) + \sqrt{D^2 i^2 + 2Ei + F^2}$ and t = thickness of membrane and

$P_B{}'$ = membrane permeability of species B

Counter-current gas Separation:

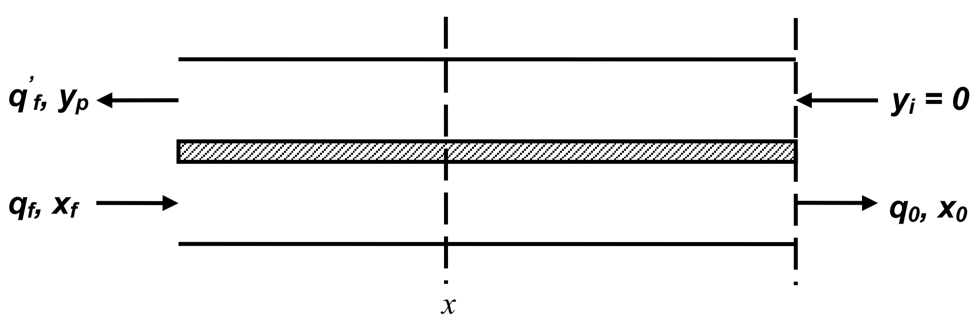


Fig. 5.4: Schematic of a counter current flow model

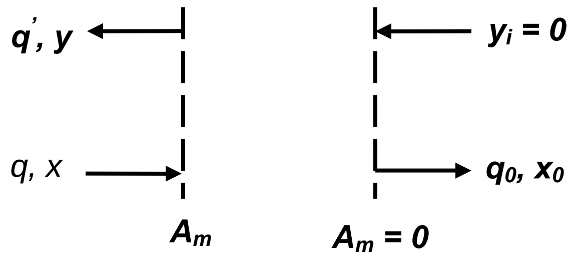


Fig. 5.5: Schematic of balance over a small element

The schematic of the counter current flow model is presented in Fig. 6.4 and the small element is shown in Fig. 5.5.

Overall material balance:

Total material in = Total material out

$$q = q_0 + q^{'} \tag{5.17}$$

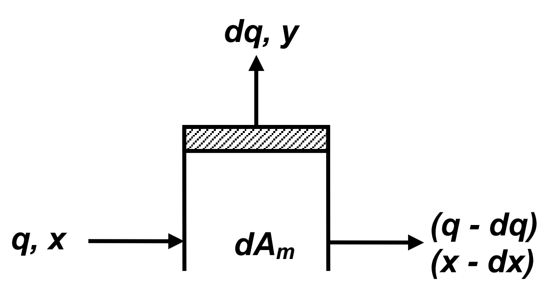
Overall A balance:

Total A in = Total A out

$$qx = q_0 x_0 + q^{'} y \tag{5.18}$$

Species A balance over a differential element,

$$d(qx) = d(q^{'} y) \tag{5.19}$$



In the above differential volume, species A balance provides,

$$qx = (q - dq)(x - dx) + ydq$$

$$ydq = d\left(qx\right) \tag{5.20}$$

Local flux of A across the membrane is presented,

$$-ydq = \frac{P_A^{'}}{t}\left[P_h x - P_l y\right] dA_m \tag{5.21}$$

For species B, the following balance equation is provided:

$$-\left(1-y\right)dq = \frac{P_B^{'}}{t}\left[P_h\left(1-x\right)-P_l\left(1-y\right)\right]dA_m \tag{5.22}$$

Combining Eqs. (5.21) and (5.22), the following expression is obtained.

$$\frac{y}{1-y} = \left(\frac{P_A^{'}}{P_B^{'}}\right)\frac{x-\left(\frac{P_l}{P_h}\right)y}{\left(1-x\right)-\left(\frac{P_l}{P_h}\right)\left(1-y\right)} \tag{5.23}$$

Eliminate $q^{'}$ by using equations (5.17) and (5.18),

$$qx = q_0 x_0 + \left(q-q_0\right)y \tag{5.24}$$

The above equation can be rearranged as

$$q_0 = q\frac{\left(x-y\right)}{\left(x_0-y\right)} \tag{5.25}$$

Bu using this equation substitute q in equation (5.21) then we get,

$$-y\frac{d\left[q_0\frac{\left(x_0-y\right)}{\left(x-y\right)}\right]}{dA_m} = \frac{P_A^{'}}{t}\left[P_h x - P_l y\right]$$

$$-yq_0\frac{d\left[\frac{x_0-y}{x-y}\right]}{dA_m} = \frac{P_A^{'}}{t}\left[P_h x - P_l y\right]$$

By derivating this equation and by rearranging it finally we get it as,

$$q_0 y\left[\left(x-x_0\right)\frac{dy}{dA_m}+\left(x_0-y\right)\frac{dx}{dA_m}\right]=\frac{P_A^{'}}{t}\left(x-y\right)\left(xP_h-yP_l\right) \tag{5.26}$$

From Eq. (5.23),

$$\frac{y}{1-y}=\alpha^*\frac{x-ry}{\left(1-x\right)-r\left(1-y\right)} \tag{5.27}$$

Where, $r=\frac{P_l}{P_h}$. The above equation is simplified as,

$$y(1-x)-r(y-y^2)=\alpha^*(1-y)(x-ry) \tag{5.28}$$

Differentiate the above equation with respect to A_m,

$$\frac{dy}{dA_m}=\left[\frac{y+\alpha^*(1-y)}{(1-x)-r(1-2y)+\alpha^*(1-y)r+\alpha^*(x-ry)}\right]\frac{dx}{dA_m}$$

$$=\beta\frac{dx}{dA_m} \tag{5.29}$$

The above equation is rearranged as,

$$\frac{dx}{dA_m}=\frac{\left(\frac{P_A^{'}}{t}\right)\left(x-y\right)\left(xP_h-yP_l\right)}{q_0 y\left[\left(x_0-x\right)-\beta\left(x,y\right)\left(x_0-y\right)\right]} \tag{5.30}$$

Similarly, the expression of $\frac{dy}{dA_m}$ can be derived.

Overall Material Balance provides,

$$q_f=q_0+q_p^{'}=q_0+\theta q_f$$

$$q_0=\left(1-\theta\right)q_f \tag{5.31}$$

Overall 'A' balance results,

$$q_f x_f=q_0 x_0+q_p^{'} y_p$$

$$y_p = \frac{x_f - (1-\theta)x_0}{\theta} \qquad (5.32)$$

For a value of given θ, then

(i) Guess x_0

(ii) Solve for y_p from equation (5.32)

(iii) Check value of y_p for solving ordinary differential equations.

(iv) Iterate.

Solved Problems

1) A membrane is used to separate a gaseous mixture A and B whose feed rate is $q_f = 10^4\ cm^3(STP)/s$ and feed composition of A, $x_f = 0.5$; The desired composition of the reject is $x_0 = 0.25$. The membrane thickness, $t = 3*10^{-3}\ cm$; P_h= feed side pressure = 80 $cm\ Hg$ and P_l = permeate side pressure = 20 $cm\ Hg$. The permeabilities are, $p_A^{'} = 60\times10^{-10}\frac{cm^3(STP).cm}{s.cm^2.cmHg}$ and $p_B^{'} = 6\times10^{-10}$ of above units. Assuming complete mixing model, calculate permeate concentration, y_p, fraction permeated θ and membrane area (A_m) required?

Solution:

x_f, x_0, α^*, P_l/P_h are given

y_p, θ, A_m are to be determined

From Eq.(), $\quad y_p = \frac{-b+\sqrt{b^2-4ac}}{2a}$

Where,

$$a = 1-\alpha^*; b = \frac{P_h}{P_l}(1-x_0) - 1 + \alpha^*\frac{P_h}{P_l}x_0 + \alpha^*$$

$$c = -\alpha^* \frac{P_h}{P_l} x_0$$

$$\alpha^* = \frac{p_A^{'}}{p_B^{'}} = \frac{60\times 10^{-10}}{6\times 10^{-10}} = 10$$

$$a = 1-\alpha^* = 1-10 = -9$$

$$b = \frac{P_h}{P_l}\left(1-x_0\right)-1+\alpha^* \frac{P_h}{P_l} x_0 + \alpha^*$$

$$= \frac{80}{20}\left(1-0.25\right)-1+10\times\frac{80}{20}\times 0.25+10$$

$$= 22$$

$$c = -\alpha^* \frac{P_h}{P_l} x_0 = -10\left(\frac{80}{20}\right)\left(0.25\right) = -10$$

$$y_p = \frac{-b+\sqrt{b^2-4ac}}{2a} = 0.604$$

$$x_0 = \frac{x_f - \theta y_p}{1-\theta}$$

$$0.25 = \frac{0.5-\theta\times 0.604}{1-\theta}$$

$$\theta = 0.706$$

$$A_m = \frac{\theta q_f y_p}{\left(p_A^{'}/t\right)\left(P_h x_0 - P_l y_p\right)} = \frac{0.706\times 10^4\times 0.604}{\left(\dfrac{60\times 10^{-10}}{3.0\times 10^{-3}}\right)\left(80\times 0.25-20\times 0.604\right)}$$

$$A_m = 2.7\times 10^8 \ cm^2$$

2) It is desired to find the membrane area required to separate air using a membrane $3*10^{-3}$ cm thickness with oxygen permeability $p_A^{'} = 300\times 10^{-10} \frac{cm^3(STP).cm}{s.cm^2.cmHg}$ and $\alpha^* = 10$ for permeability ratio of oxygen to nitrogen. Feed rate, $q_f = 2\times 10^6 \ cm^3(STP)/s$ and fraction

cut $\theta = 0.20$; $P_h = 200\ cm\ Hg$ and $P_l = 20\ cm\ Hg$. Assume, complete mixing model, calculate permeate composition, reject composition and membrane area?

Solution:

$x_f = 0.21$ (mole fraction of oxygen in air)

$$a_1 = \theta + \frac{P_l}{P_h} - \frac{P_l}{P_h}\theta - \alpha^*\theta - \alpha^*\frac{P_l}{P_h} + \alpha^*\frac{P_l}{P_h}\theta$$

$$= 0.2 + \frac{20}{200} - \frac{20}{200}\times 0.2 - 10\times 0.2 - 10\times\frac{20}{200} + 10\times\frac{20}{200}\times 0.2$$

$$= 0.2 + 0.1 - 0.02 - 2 - 1 + 0.2$$

$$= -2.52$$

$$b_1 = 1 - \theta - x_f - \frac{P_l}{P_h} + \frac{P_l}{P_h}\theta + \alpha^*\theta + \alpha^*\frac{P_l}{P_h} - \alpha^*\frac{P_l}{P_h}\theta + \alpha^* x_f$$

$$= 1 - 0.2 - 0.21 - \frac{20}{200} + \frac{20}{200}\times 0.2 + 10\times 0.2 + 10\times\frac{20}{200} - 10\times\frac{20}{200}\times 0.2 + 10\times 0.21$$

$$= 1 - 0.2 - 0.21 - 0.1 + 0.02 + 2 + 1 - 0.2 + 2.1$$

$$= 5.41$$

$$c_1 = -\alpha^* x_f = -10\times 0.21 = -2.1$$

$$y_p = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{-5.41 + \sqrt{5.41^2 - 4\times 2.52\times(-2.1)}}{2\times(-2.52)}$$

$$= 0.509$$

$$x_0 = \frac{x_f - \theta y_p}{1-\theta} = \frac{0.21 - 0.2\times 0.509}{1 - 0.2} = 0.135$$

$$A_m = \frac{\theta q_f y_p}{\left(p_A^{'}/t\right)\left(P_h x_0 - P_l y_p\right)}$$

$$= \frac{0.2\times 2\times 10^6\times 0.509}{\left(\dfrac{300\times 10^{-10}}{3\times 10^{-3}}\right)\left(200\times 0.135 - 20\times 0.509\right)}$$

$$= 1.21\times 10^9\ cm^2$$

References:

1. C. J. Geankoplis, Transport Processes and Unit Operations, Prentice Hall of India, New Delhi,1997.