THE CORRECT FORMULATION OF PROBLEMS PERTAINING TO THE CONVECTIVE DIFFUSION OF SALTS IN FINITE POROUS MEDIA

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The refined boundary condition at the inlet of a system has been formulated with consideration given to the effect of the boundedness of the volume of the pressurized container; an engineering solution of the problem is presented with respect to a typical experimental set-up [1–3].

In the theoretical analysis of a typical experimental set-up for investigation of the process of convective diffusion of salts [1–3] it is generally assumed that the concentration value at the inlet to the system is constant; in particular, in studying the distillation process it is assumed that $c(0, t) = 0$.

Generally speaking, this condition is possible only in the limiting case in which a solvent is fed to the system's inlet from an infinitely large and thoroughly mixed pressurized container.* The distillation of a finite medium under these circumstances comes about for two reasons: the discharging solution produces macrotransport at the outlet face; microtransport occurs at the inlet face (toward the filtration flow) because of the diffusion of the salts.

An observer standing at the outlet face of the system will clearly be able to establish the difference between the initial quantity of salts dissolved in the medium and the amount removed (within an infinite period of time). The magnitude of this difference has been evaluated in [3] and can be used to determine the effective Pe(clet) numbers.

Unlike the real limit condition, constancy of concentration at the system's inlet need not be maintained. Indeed, since the volume of the liquid within the pressurized container is finite (and constant, because of continuous replacement), the diffusion flow from the medium into the pressurized container changes the initial zero value of the concentration to the final value. During the course of the experiment, the value of the concentration within the pressurized container will rise from zero to some maximum value, subsequently tending toward zero, in proportion to the speed with which the liquid in the pressurized container is continuously replaced with pure solvents.

Under these circumstances the dissolved salts diffusing into the pressurized container will obviously no longer be irreversibly lost to an observer standing at the outlet face. In the final analysis, such an observer will be able to establish the total quantity of salts removed from the medium being studied; it is obvious in this case that the time for the virtually complete distillation is somewhat greater than in the limit case in which an infinitely large pressurized container is used.

Let us formulate the problem. We have a porous rod filled with a solution of a uniform concentration. A pressurized container filled with a pure solvent provides a flow of a liquid to the inlet of the system (the rod). It is assumed that mixing takes place within the pressurized container; in particular, this can be accomplished through the continuous inflow of additional solvent. The outlet face of the rod is in contact with the air; consequently, there is no diffusion flow there. The quantity of salt Q(t) removed from the medium is what we have to measure. Knowing Q(t), we have to describe the expulsion process.

The distribution of the salts in the rod is described by the solution of the convective-diffusion equation

$$\frac{\partial c}{\partial n} + \frac{\partial c}{\partial y} = \frac{1}{\mathrm{Pe}} \frac{\partial^2 c}{\partial y^2} \tag{1}$$

under the following conditions:

$$c(y, 0) = 1, \tag{2}$$

$$c(0, n) = a(n), \tag{3}$$

$$a(0) = 0, \tag{4}$$

$$-\frac{da}{dn} = \beta\left[a(n) - \frac{1}{\mathrm{Pe}} \frac{\partial c(0,n)}{\partial y}\right], \tag{5}$$

$$\frac{\partial c(1, n)}{\partial y} = 0. \tag{6}$$

Conditions (2)–(4) and (6) are obvious. Condition (5) expresses the circumstance that the change in the amount of salts within the pressurized container is governed by the difference between the amount of salt removed from the container by the liquid entering the rod and the amount diffusing from the rod into the container. Since the positive direction of the over-all flow corresponds to the loss $a(n)$, we have chosen the "minus" sign in (5).

We note that as $\beta \to 0$ (this corresponds to the case of an infinitely large pressurized container), considering (4), from condition (5) we have $c(0, n) = 0$, i.e., a variant considered in [1–3]. As $\beta \to \infty$ (this corresponds to the case of an infinitely small pressurized container), we find that $c(0, n) - (1/\mathrm{Pe}) \times$ $\times\ \partial c(0, n)/\partial y = 0$, i.e., a variant considered in [4].

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*Other means of satisfying this condition are possible. In particular, when the inlet of the system is streamlined by a liquid of adequate height (to produce the pressure that is needed), etc.

For the value of Q(n) of interest to us, we have

$$Q(n) = mlS \int_0^n c(1, \tau)\, d\tau. \tag{7}$$

It is not difficult to see that the system of equations (1)–(6) provides for the complete removal from the face y = 1 of the salts initially contained within the rod. Indeed, having integrated Eq. (1) with respect to y in limits from zero to unity, we obtain

$$\frac{d}{dn}\int_0^1 c(y, n)\, dy + c(1, n) - c(0, n) =$$

$$= \frac{1}{\mathrm{Pe}}\frac{\partial c(1, n)}{dy} - \frac{1}{\mathrm{Pe}}\frac{\partial c(0, n)}{\partial y}. \tag{8}$$

With consideration of conditions (2)–(6), let us rewrite Eq. (8) in the form

$$c(1, n) = -\frac{d}{dn}\left[\frac{a(n)}{\beta} + \int_0^1 c(y, n)\, dy\right]. \tag{9}$$

Bearing in mind Eq. (7), we find that

$$Q(n) = -mlS\left[\frac{a(n)}{\beta} + \int_0^1 c(y, n)\, dy\right]_{n=0}^{n}, \tag{10}$$

from which

$$Q(\infty) = mlS, \tag{11}$$

which is what we had to prove.

Let us turn to the solution of system (1)–(6). Applying the Laplace-Carson transform (with respect to the variable n) to Eqs. (1)–(6), we find the solution for the transformed equation (1) in the form

$$\bar{c}(y, p) =$$

$$= 1 + A\exp\left[\frac{\lambda - d}{2}\, y\right] + B\exp\left[-\frac{\lambda + d}{2}\, y\right]. \tag{12}$$

Using the transformed conditions (2)–(6), we obtain

$$B = (p + \beta)\Big[\varphi(p)(p + \beta)(\lambda - d)^{-1} +$$

$$+ \beta(\lambda + d)[1 - \exp(-\lambda)]/2\mathrm{Pe}\Big]^{-1}, \tag{13}$$

$$A = B\,\frac{\lambda + d}{\lambda - d}\exp(-\lambda), \tag{14}$$

where

$$\varphi(p) \equiv (\lambda - d) + (\lambda + d)\exp(-\lambda), \tag{15}$$

$$d \equiv -\mathrm{Pe};\ \lambda \equiv \sqrt{\mathrm{Pe}^2 + 4\,\mathrm{Pe}\, p}. \tag{16}$$

For the value of $\bar{c}(1, p)$ of interest to us, we find that

$$\bar{c}(1, p) =$$

$$= 1 - 2\lambda\,\frac{(p + \beta)\exp\left[-\frac{\lambda + d}{2}\right]}{\varphi(p)(p + \beta) + 2p\beta[1 - \exp(-\lambda)]}. \tag{17}$$

Applying the theorem of operator expansion [5], we easily find the expression for the preimage of c(1, n):

$$c(1, n) = -16\,\mathrm{Pe}\exp(\mathrm{Pe}/2) \times$$

$$\times \sum\left(\alpha_r^2\exp\left[-\frac{4\alpha_r^2 + \mathrm{Pe}^2}{4\,\mathrm{Pe}}\, n\right]\right)(4\alpha_r^2 + \mathrm{Pe}^2)^{-1} \times$$

$$\times\left[\mathrm{Pe}(2 + \mathrm{Pe}) + 2\,\mathrm{Pe}\, y_r(\beta) + 4\alpha_r^2\frac{\mathrm{Pe} + x_r(\beta)}{\mathrm{Pe} + 2y_r(\beta)}\right]^{-1} \times$$

$$\times(\cos\alpha_r)^{-1}; \tag{18}$$

where

$$x_r(\beta) = \frac{2\beta^2}{(p_r + \beta)^2},$$

$$y_r(\beta) = \frac{p_r\beta}{p_r + \beta},\ p_r = -\frac{4\alpha_r^2 + \mathrm{Pe}}{4\,\mathrm{Pe}}, \tag{19}$$

while the values of α_r are determined from the equation

$$\operatorname{ctg}\alpha_r = -\frac{\mathrm{Pe}}{2\alpha_r} - \frac{(4\alpha_r^2 + \mathrm{Pe}^2)\beta}{(4\alpha_r^2 + \mathrm{Pe}^2 - 4\,\mathrm{Pe}\,\beta)\alpha_r}. \tag{20}$$

When $\beta = 0$, we can easily derive the expression familiar from [2, 3] from formula (18).

Equation (18) is exact. Looking for convenient calculational formulas, let us turn to certain simplifications and, namely, let us restrict ourselves to a consideration of the case $\mathrm{Pe} \ge 2$, which is of greatest practical interest.

Under these circumstances the expression for $\varphi(p)$ can be replaced by the approximate relationship $\varphi(p) \approx \approx \lambda - d$ and, retaining the adapted degree of accuracy, we can rewrite Eq. (17) as follows:

$$\bar{c}(1, p) = 1 - 2\lambda\,\frac{\exp\left[\frac{\lambda + d}{2}\right](p + \beta)}{(p + \beta)(\lambda - d) + 2p\beta}. \tag{21}$$

Subsequently we find that the relationship

$$(p + \beta)(\lambda - d) \gg 2p\beta \tag{22}$$

is valid since $\beta \ll 1$ (for the conditions of the experiment described in [1–3]).

With consideration of the foregoing, we can replace (21) with the following, retaining extremely high accuracy:

$$\bar{c}(1, p) = \bar{c}^{+}(1, p) + \Delta\bar{c}(1, p), \tag{23}$$

where

$$\bar{c}^{+}(1, p) = 1 - 2\lambda\,\frac{\exp\left[-\frac{\lambda + d}{2}\right]}{\lambda - d}, \tag{24}$$

$$\Delta\bar{c}(1, p) = \frac{2\beta\exp(\mathrm{Pe}/2)}{\sqrt{\mathrm{Pe}}}\,\frac{p}{p + \beta}\,F(p), \tag{25}$$

$$F(p) = \frac{\sqrt{p + \varepsilon}\,\exp[-\sqrt{\alpha(p + \varepsilon)}]}{(\sqrt{p + \varepsilon} + \sqrt{\varepsilon})^2}$$

$$(\varepsilon = \mathrm{Pe}/4,\ \alpha = \mathrm{Pe}). \tag{26}$$

We write the expression for $\bar{Q}(p)$ in similar fashion:

$$\bar{Q}(p) = \bar{Q}^{+}(p) + \Delta\bar{Q}(p), \tag{27}$$

where

$$\bar{Q}^{+}(p) = mlS\,\bar{c}^{+}(1, p)/p; \tag{28}$$

$$\Delta\bar{Q}(p) = mlS\,\Delta\bar{c}(1, p)/p. \tag{29}$$

The values of $\bar{c}^{+}(1, p)$ and $\bar{Q}^{+}(p)$ correspond to $\beta = 0$. The corresponding preimages were determined earlier in [3] and have the form

$$\begin{aligned} c^{+}(1,n) &= \\ = 1 - 2\exp(2\sqrt{\alpha\varepsilon})&\left\{\operatorname{erfc}\xi\left(\frac{3}{4} + \frac{\mathrm{Pe}}{4} + \frac{\mathrm{Pe}\,n}{4}\right) - \right. \\ &- \frac{\sqrt{\varepsilon n}}{\sqrt{\pi}}\exp(-\sqrt{\alpha\varepsilon})\exp\left(-\frac{\alpha}{4n} - \varepsilon n\right) + \\ &\left. + \frac{1}{4}\exp(-2\sqrt{\alpha\varepsilon})\operatorname{erfc}\eta\right\}, \end{aligned} \tag{30}$$

$$\begin{aligned} Q^{+}(n) = mlS&\left\{n - \left(\frac{n}{2} + \frac{1}{2\,\mathrm{Pe}} - \frac{1}{2}\right)\operatorname{erfc}\eta - \right. \\ &- \exp(2\sqrt{\alpha\varepsilon})\operatorname{erfc}\xi \times \\ &\times \left[\frac{\mathrm{Pe}\,n^{2}}{4} + \frac{3\,\mathrm{Pe}}{2}n + \frac{\mathrm{Pe}^{2}/2 + 2\,\mathrm{Pe} - 1}{2\,\mathrm{Pe}}\right] + \\ &+ \left[\frac{n\sqrt{\mathrm{Pe}\,n}}{2} + \right. \\ &\left.\left. + \frac{1 + \mathrm{Pe}/2}{\sqrt{\mathrm{Pe}}}\sqrt{n}\right]\frac{\exp(-\eta^{2})}{\sqrt{\pi}}\right\} \end{aligned}$$

$$\left(\xi = \frac{1}{2}\sqrt{\frac{\alpha}{n}} + \sqrt{\varepsilon n},\ \ \eta = \frac{1}{2}\sqrt{\frac{\alpha}{n}} - \sqrt{\varepsilon n}\right). \tag{31}$$

Let us return to the determination of the correction factors which describe the effect of the boundedness of the pressurized container. Let us introduce into our consideration the tabulated transform [5]:

$$f(p) = \frac{p\sqrt{p+\varepsilon}\exp[-\sqrt{\alpha(p+\varepsilon)}\,]}{(p+\beta)(b+\sqrt{p+\varepsilon})}. \tag{32}$$

Having differentiated the preimage corresponding to the transform in the form of (32), on the basis of b—and subsequently assuming that b = √ε—we find the preimage which corresponds to a transform in the form of (25). Thus we obtain

$$\begin{aligned} &\frac{\sqrt{\mathrm{Pe}}\,\Delta c(1,n)}{2\beta\exp(\mathrm{Pe}/2)} = \\ &= \frac{\sqrt{\varepsilon-\beta}}{2}\exp(-\beta n)\frac{\exp[-\sqrt{\alpha(\varepsilon-\beta)}]}{(\sqrt{\varepsilon} + \sqrt{\varepsilon-\beta})^{2}} \times \\ &\times \operatorname{erfc}\left[\frac{1}{2}\sqrt{\frac{\alpha}{n}} - \sqrt{(\varepsilon-\beta)n}\right] + \\ &+ \frac{2\varepsilon\sqrt{n}}{\beta\sqrt{\pi}}\exp\left(-\frac{\alpha}{4n} - \varepsilon n\right) - \\ &- \exp(\sqrt{\alpha\varepsilon})[2\sqrt{\varepsilon} + \\ &+ \varepsilon\sqrt{\alpha} + 2\varepsilon n\sqrt{\varepsilon}\,]\operatorname{erfc}\xi - \frac{1}{\beta^{2}} \times \\ &\times \left\{\frac{\sqrt{\varepsilon-\beta}}{2}(\sqrt{\varepsilon} + \right. \\ &+ \sqrt{\varepsilon-\beta})^{2}\exp(-\beta n)\exp[\sqrt{\alpha(\varepsilon-\beta)}] \times \\ &\times \operatorname{erfc}\left[\frac{1}{2}\sqrt{\frac{\alpha}{n}} + \sqrt{(\varepsilon-\beta)n}\right] - \\ &\left. - 2\varepsilon\sqrt{\varepsilon}\exp(\sqrt{\alpha\varepsilon})\operatorname{erfc}\xi\right\}. \end{aligned} \tag{33}$$

Equation (33) can be substantially simplified, since $\beta \ll \varepsilon$ (=Pe/4). Expanding the quantities within the braces with respect to β (retaining terms to β^{2} inclusively), and omitting the tedious calculations, we obtain

$$\begin{aligned} &\frac{\sqrt{\mathrm{Pe}}\,\Delta c(1,n)}{2\beta\exp(\mathrm{Pe}/2)} = \\ &= \frac{\exp(-\sqrt{\alpha\varepsilon})}{8\sqrt{\varepsilon}}\exp(-\beta n)\operatorname{erfc}\eta + \\ &+ \frac{\sqrt{n}}{\sqrt{\pi}}\exp\left(-\frac{\alpha}{4n} - \varepsilon n\right)\left[\varepsilon n + \frac{3 + \sqrt{\varepsilon\alpha}}{2}\right] - \\ &- \left[\varepsilon\sqrt{\varepsilon}\,n^{2} + \right. \\ &+ n(2\sqrt{\alpha\varepsilon} + \varepsilon\sqrt{\alpha}) + \frac{3\sqrt{\alpha}}{4} + \\ &\left. + \frac{\alpha\sqrt{\varepsilon}}{4} + \frac{1}{8\sqrt{\varepsilon}}\right] \times \\ &\times \exp(-\sqrt{\alpha\varepsilon})\operatorname{erfc}\xi. \end{aligned} \tag{34}$$

For large Pe numbers we can use the simpler expression

$$\Delta l(1,n) = \frac{\beta\exp(-\beta n)}{2\,\mathrm{Pe}}\operatorname{erfc}\eta. \tag{35}$$

Let us now turn to the determination of $\Delta Q(n)$. First we rewrite Eq. (29), with consideration of (25), in the form

$$\begin{aligned} &\Delta Q(p) = \\ &= 2mlS\frac{\exp(\mathrm{Pe}/2)}{\sqrt{\mathrm{Pe}}}\left[F(p) - \frac{p}{p+\beta}F(p)\right]. \end{aligned} \tag{36}$$

The preimage which corresponds to the second term in the brackets was cited above. The preimage which corresponds to the first term is obviously a special value of the expression known for $\beta = 0$.

Omitting the simple but tedious calculations, we obtain

$$\Delta Q(n) = mlS[1 - \exp(-\beta n)]\operatorname{erfc}\eta/2\,\mathrm{Pe}. \tag{37}$$

Relationships (35) and (37) are convenient formulas with which to work. It is curious to note that the structure of the correction factors $\Delta c(1, n)$ and $\Delta Q(n)$ is entirely analogous to the structure of the correction factors which describe the effect of skeletal sorption.

Considering (31) and (37), for the complete removal of the salts over an infinite period of time we find a value of

$$Q(\infty) = mlS(1 - 1/\mathrm{Pe}) + mlS/\mathrm{Pe} = mlS, \tag{38}$$

which is exactly equal to the quantity required.

It was demonstrated in [3] that assuming the condition $c(0, t) = 0$ (see above), the theory leads to complete distillation at $n \leq 2$ ($\mathrm{Pe} > 2$), which is not always in agreement with experiment. The overcoming of this contradiction necessarily involves consideration both of the skeletal sorption of the medium (for active media) and the existence of closed pores. We have carried out such an analysis in various studies.

In this paper we sought to draw attention to the fact that for values of β not too small even the "classical" theory of convective diffusion of salts in inert and homogeneous media makes it possible "to retard" the distillation process.

Thus, for values of $\beta \approx 10^{-1}$–10^{-2}, $\mathrm{Pe} \approx 10$–10^2, and $n \approx 5$–10 for $\Delta c(1, n)$ we have $\Delta c(1, n) \approx 10^{-2}$–$10^{-4}$ (from an initial value of $c(x, 0)$), which is a completely measurable quantity denoting the error of the theory using the condition $c(0, t) = 0$.

In conclusion, let us note that the condition $c(0, t) = 0$ will be satisfied exactly for any β if the experiment is set up so as to provide for a sink (at the point at which the medium under investigation comes into contact with the pressurized container) or at the point at which it comes into contact with a hose that leads to the pressurized container). The existence of this sink (naturally offset by the addition of a pure solvent into the container) makes it possible to regard the concentration within the container as constant, in view of the ejection to the outside of the salts being diffused into the container.

NOTATION

c is the solution concentration in the pore space of the rod; a is the solution concentration in the pressurized container; v is the mean velocity of liquid flow in pores; D is the diffusion coefficient per unit surface of pore space; m is the porosity value; l is the rod length; S is the cross sectional area of the body; w_c is the volume of the pressurized container; $w_r = mlS$ is the volume of pore space of the rod; $n = vt/l$; $y \equiv x/l$, $\beta = w_r/w_c$ $\mathrm{Pe} = vl/D$ is the amount of liquid flowing out of the rod, expressed in units of pore space volume.

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