3. B. I. Kitaev, Yu. G. Yaroshenko, and B. P. Lazarev, Heat Exchange in Blast Furnaces [in Russian], Metallurgiya, Moscow (1966).
4. V. I. Koloberdin, V. N. Blinichev, and V. V. Strel'tsov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 14, 1276 (1971).
5. D. K. Kollerov, Inzh.-Fiz. Zh., 2, No. 8 (1959).
6. N. P. Tabunshchikov, Khim. Prom-st', No. 3 (1956).
7. D. M. Ginzburg, Khim. Prom-st', No. 6 (1959).
8. R. E. Krzhizhanovskyi and Z. Yu. Shtern, Thermophysical Properties of Nonmetallic Materials [in Russian], Énergiya, Leningrad (1973).
9. J. Wuhrer, Chem. Ing. Tech., No. 1, 19 (1958).
10. N. P. Tabunshchikov, in: Study of Shaft Lime Kilns [in Russian], Khimiya, Leningrad (1964), p. 52.
11. A. M. Aizen, N. P. Tabunshchikov, I. M. Fedotkin, and N. N. Marutovskaya, Izv. Vyssh. Uchebn. Zaved., Chern. Metallurg., 39, No. 10 (1974).
12. N. A. Livshin and V. N. Pugachev, Stochastic Analysis of Automatic Control Systems [in Russian], Sov. Radio, Moscow (1963).
13. A. Hald, Statistical Theory with Engineering Applications, Wiley (1952).
14. Ya. Yanko, Mathematical Statistical Tables [in Russian], Gosstatizdat, Moscow (1961).

TRANSIENT RESPONSE OF A THERMAL-DIFFUSION COLUMN WITH BUFFER VESSELS AT THE ENDS

G. D. Rabinovich, V. M. Dorogush,
and A. V. Suvorov

UDC 621.039.3

The transient response in a column with buffer vessels at the ends has been determined for the approximation $c(1-c) = a + bc$, and this is compared with the asymptotic solution for small times; the range of application of the latter has been determined.

Asymptotic solutions have been derived [1, 2] for the transient response in a thermal-diffusion column with buffer vessels at the ends for two ways of approximating the nonlinear term in the transport equation, namely, $c(1-c) \approx a$ and $c(1-c) \approx c$; it was found that these asymptotic solutions can themselves be approximated very closely by linear relationships of the form

$$\frac{\Delta c}{\tau} = p - r\sqrt{\tau}, \tag{1}$$

in which p and r are coefficients to be determined from experiment and which allow one to calculate the Soret coefficient. However, uncertainty arises as to the time range in which each of the asymptotic solutions applies when this method is used.

The problem has been solved by deriving an exact solution, which is then compared with the asymptotic one. The problem is formulated [3] as follows: we have the differential equation

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial y^2} - \frac{\partial [c(1-c)]}{\partial y} \tag{2}$$

to be solved subject to the boundary conditions

$$c|_{\theta=0} = c_0 \quad (y > 0), \tag{3}$$

$$y_e \omega_i \left.\frac{\partial c}{\partial \theta}\right|_{y=0} = \left[\frac{\partial c}{\partial y} - c(1-c)\right]_{y=0} \quad (\theta > 0), \tag{4}$$

Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 3, pp. 447-452, March, 1976. Original article submitted February 4, 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $7.50.

$$y_e\omega_e \left.\frac{\partial c}{\partial \theta}\right|_{y=y_e} = \left[c(1-c)-\frac{\partial c}{\partial y}\right]_{y=y_e} \quad (\theta > 0). \tag{5}$$

Since (4) and (5) contain a nonlinear term, an exact solution cannot be obtained, but there is a method based on the following approximation first used in [4]:

$$c(1-c) = a + bc, \tag{6}$$

which for concentration differences $\Delta c \equiv c_k - c_0 \leq 0.03$ gives an error less than 1% in the range $0.01 < c_0 < 0.99$, with

$$a = c_0 c_k;\; b = 1 - c_0 - c_k. \tag{6a}$$

The concentration shifts in fact lie within the above limits in measurements on the Soret coefficient, so the substitution of (6) can be made in (4) and (5).

The problem was solved in [5] in this formulation but the results contained errors.

We introduce the new variables

$$u = c - c_0;\; y^* = by;\; \theta^* = b^2\theta, \tag{7}$$

to put (2)-(5) with (6) in the form

$$\frac{\partial y}{\partial \theta^*} = \frac{\partial^2 u}{\partial y^{*2}} - \frac{\partial y}{\partial y^*}, \tag{8}$$

$$y_e^*\omega_i \left.\frac{\partial u}{\partial \theta^*}\right|_{y^*=0} = \left(\frac{\partial u}{\partial y^*} - u\right)_{y^*=0} - \frac{c_0(1-c_0)}{b}, \tag{9}$$

$$y_e^*\omega_e \left.\frac{\partial u}{\partial \theta^*}\right|_{y^*=y_e^*} = \left(u - \frac{\partial u}{\partial y^*}\right)_{y^*=y_e^*} + \frac{c_0(1-c_0)}{b}, \tag{10}$$

$$u|_{\theta^*=0} = 0. \tag{11}$$

Laplace — Carson integral transformations are used with (9)-(11) to get the solution to (8) in the following form:

$$\begin{aligned} \bar{u} = \frac{c_0(1-c_0)}{bp}\, e^{\frac{y^*}{2}} \Big\{ & e^{-\frac{y_e^*}{2}} \left[\lambda \operatorname{ch} \lambda y^* + \left(\frac{1}{2} + y_e^*\omega_i p\right) \operatorname{sh} \lambda y^*\right] - \\ & - \lambda \operatorname{ch} \lambda (y_e^* - y^*) + \left(\frac{1}{2} - y_e^*\omega_e p\right) \operatorname{sh} \lambda (y_e^* - y^*)\Big\} \times \\ \times \Big\{ & \lambda y_e^* (\omega_e + \omega_i) \operatorname{ch} \lambda y_e^* + \left[1 + \frac{1}{2} y_e^* (\omega_e - \omega_i) + y_e^{*2}\omega_i\omega_e p\right] \operatorname{sh} \lambda y_e^* \Big\}^{-1}, \end{aligned} \tag{12}$$

where

$$\lambda = \sqrt{p + \frac{1}{4}}, \tag{13}$$

and p is an operator.

Consider the case where one of the vessels at the end of the column is very large, i.e., we put $\omega_i \to \infty$ or $\omega_e \to \infty$ in (12); then for the positive end $(y^* = y_e^*)$ we get instead of (12)

$$\bar{u}_e = \frac{c_0(1-c_0)}{b} \cdot \frac{\operatorname{sh} \lambda y_e^*}{\lambda \operatorname{ch} \lambda y_e^* + \left(y_e^*\omega_e p - \frac{1}{2}\right) \operatorname{sh} \lambda y_e^*}, \tag{14}$$

and for the negative end $(y^* = 0)$

$$\bar{u}_i = \frac{c_0(1-c_0)}{b} \cdot \frac{\operatorname{sh} \lambda y_e^*}{\lambda \operatorname{ch} \lambda y_e^* + \left(y_e^*\omega_i p + \frac{1}{2}\right) \operatorname{sh} \lambda y_e^*}. \tag{15}$$

We introduce the symbols

$$\frac{1}{y_e^*\omega_e} + \frac{1}{2} = k, \quad x = \left(k - \frac{1}{2}\right)^2 \theta^*, \tag{16}$$

$$v_e = \frac{bu_e}{c_0(1-c_0)} \cdot \frac{2k-1}{2x} \tag{17}$$

and transfer from the transform in (15) to the original via the expansion theorem to get

$$v_e = \frac{2k-1}{2x}\left\{\exp\left[\frac{1}{\omega_e(2k-1)}\right]-1\right\} + \frac{2\omega_e^2(2k-1)^2}{x}\sum_n \frac{r_n^2 \operatorname{sh} r_n \exp x\left[r_n^2\omega_e^2 - \frac{1}{(2k-1)^2}\right]}{[(2k-1)^2\omega_e^2 r_n^2 - 1]\,C_n}, \tag{18}$$

where

$$C_n = \left[r_n^2\omega_e^2 - \frac{2k}{(2k-1)^2}\right] r_n \operatorname{ch} r_n + \left[r_n^2\omega_e(1+\omega_e) + \frac{2k}{(2k-1)^2}\right]\operatorname{sh} r_n, \tag{19}$$

and the roots r_n are defined by

$$\operatorname{th} r_n = \frac{(2k-1)^2\omega_e r_n}{2k-(2k-1)^2\omega_e^2 r_n^2}. \tag{20}$$

We see from (20) that there are only imaginary roots for $k < 0$, whereas the purely imaginary roots are accompanied by one real root if $\omega_e(2k-1)^2/2k < 1$; the summation in (18) must be taken over all roots.

We now find the asymptotic solutions for small times from (14) and (15).

If the times are small (p is large) and if y_e^* is not too small, we can [1] put

$$\operatorname{ch}\lambda y_e^* \approx \operatorname{sh}\lambda y_e^*. \tag{21}$$

Then after certain steps we get

$$\bar{u}_e = \frac{c_0(1-c_0)}{b(1+y_e^*\omega_e)}\left(\frac{1}{\sqrt{p+\frac{1}{4}}-\frac{1}{2}} - \frac{1}{\sqrt{p+\frac{1}{4}+\frac{1}{y_e^*\omega_e}}+\frac{1}{2}}\right), \tag{22}$$

$$\bar{u}_i = -\frac{c_0(1-c_0)}{b(1-y_e^*\omega_i)}\left(\frac{1}{\sqrt{p+\frac{1}{4}}+\frac{1}{2}} - \frac{1}{\sqrt{p+\frac{1}{4}+\frac{1}{y_e^*\omega_i}}-\frac{1}{2}}\right). \tag{23}$$

We revert to the originals in (22) and (23) and use (16) and (17) to get

$$\begin{aligned} v = {} & \frac{1}{\pm 2k+1} - \frac{\pm 2k(\pm 2k-1)}{(\pm 2k+1)^2 x} + \frac{\pm 2k-1}{\pm 2k+1}\left[\frac{1}{\pm 2k-1} + \frac{4k^2+1}{2x(\pm 2k+1)}\right] \times \\ & \times \operatorname{erf}\left(\frac{\sqrt{x}}{\pm 2k-1}\right) + \frac{\pm 2k-1}{\pm 2k+1}\sqrt{\frac{x}{\pi}}.\exp-\left[\frac{x}{(\pm 2k-1)^2}\right] + \\ & + \frac{\pm 2k(\pm 2k-1)}{(\pm 2k+1)^2}\exp\left(\frac{\pm 2k+1}{\pm 2k-1}x\right)\operatorname{erfc}\left(\frac{\pm 2k}{\pm 2k-1}\sqrt{x}\right), \end{aligned} \tag{24}$$

where the plus sign relates to the positive end of the column and the minus sign, to the negative one, with

$$v = \frac{bu}{c_0(1-c_0)} \cdot \frac{\pm 2k-1}{2x} \tag{25}$$

and variable u must be given the subscript e or i as appropriate.

If we put $x = 0$ in (24), we get $v = 1$, while for the case $b = 0$, which corresponds in accordance with (7) and (16) to $k \to \infty$, we get an expression given in [1] by resolving the indeterminacy:

$$v = \frac{2}{\sqrt{\pi x}} - \frac{1}{x}\left(1 - e^x \operatorname{erfc}\sqrt{x}\right). \tag{26}$$

We now find from (12) expressions for the concentration changes at the positive and negative ends for a column having vessels of finite size at the ends and for small times, i.e., subject to the condition of (21); after simple steps we get expressions identical with (22)-(24).

Then for small times corresponding to the condition of (21) the concentration change at either end is independent of the change at the other end; however, in that case, a difference from the solution of [5] is that the changes will not be symmetrical, i.e., $|u_e| \neq |u_i|$.

TABLE 1. Values of v as a Function of Dimensionless Time x and Dimensionless Volume ω for Various Values of $y_e^* \omega_e$

ω	x									
	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
$y_e^*\omega_e = 2$										
0,500	0,815	0,787	0,768	0,754	0,743	0,735	0,728	0,723	0,718	0,714
1,000	0,832	0,796	0,773	0,757	0,743	0,731	0,721	0,711	0,701	0,692
2.000	0,833	0,786	0,746	0,711	0,678	0,648	0,619	0,592	0,567	0,544
From (24)	0,836	0,797	0,775	0,759	0,747	0,738	0,731	0,725	0,720	0,716
$y_e^*\omega_e = \frac{2}{3}$										
0,300	0,834	0,771	0,733	0,706	0,684	0,667	0,652	0,639	0,628	0,618
0,400	0,827	0,768	0,731	0,704	0,683	0,666	0,651	0,638	0,627	0,617
1,000	0,816	0,762	0,727	0,699	0,676	0,656	0,637	0,620	0,604	0,588
2,000	0,814	0,751	0,699	0,653	0,611	0,574	0,539	0,508	0,480	0,453
3,000	0,803	0,715	0,641	0,577	0,523	0,476	0,434	0,399	0,367	0,340
From (24)	0,815	0,762	0,727	0,701	0,680	0,664	0,649	0,637	0,626	0,616
$y_e^*\omega_e = \frac{1}{4}$										
0,200	0,805	0,748	0,709	0,680	0,656	0,636	0,619	0,604	0,591	0,579
0,300	0,807	0,749	0,710	0,681	0,657	0,637	0,619	0,604	0,591	0,579
0,400	0,810	0,751	0,711	0,681	0,657	0,637	0,620	0,605	0,591	0,579
0,500	0,810	0,750	0,711	0,681	0,657	0,637	0,620	0,605	0,591	0,579
1,000	0,808	0,749	0,710	0,679	0,652	0,629	0,608	0,588	0,569	0,552
2,000	0,807	0,739	0,682	0,633	0,589	0,550	0,514	0,482	0,453	0,426
From (24)	0,808	0,749	0,710	0,681	0,657	0,637	0,619	0,604	0,591	0,579
$y_e^*\omega_e = -6$										
0,300	0,683	0,537	0,436	0,362	0,307	0,265	0,231	0,205	0,183	0,166
0,400	0,683	0,537	0,436	0,362	0,307	0,265	0,231	0,205	0,183	0,166
0,500	0,683	0,537	0,436	0,362	0,307	0,265	0,231	0,205	0,183	0,166
1,000	0,685	0,537	0,436	0,362	0,307	0,264	0,231	0,204	0,183	0,165
2,000	0,683	0,533	0,429	0,353	0,297	0,255	0,222	0,196	0,175	0,158
3,000	0,676	0,617	0,408	0,331	0,276	0,235	0,203	0,179	0,160	0,144
From (24)	0,683	0,537	0,436	0,362	0,307	0,265	0,231	0,205	0,183	0,165
$y_e^*\omega = -8$										
0,200	0,640	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125
0,300	0,640	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125
0,400	0,640	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125
0,500	0,640	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125
1,000	0,639	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125
2,000	0,640	0,472	0,363	0,290	0,239	0,202	0,174	0,153	0,136	0,123
3,000	0,635	0,461	0,351	0,278	0,228	0,192	0,165	0,145	0,129	0,116
From (24)	0,640	0,474	0,367	0,294	0,243	0,205	0,177	0,156	0,139	0,125

The solution of (18) was used for comparison with the results given by (24); a computer was used to calculate the roots of (20) and the values of v from (18) and (24). The latter are given in Table 1, which shows that for $y_e^* \omega_e > 0$ any increase in this parameter reduces the range in ω for which the solution to (24) agrees well with (18) up to the values $x = 1$. On the other hand, in the region $y_e^* \omega_e < 0$, the two solutions are virtually coincident up to $\omega \approx 2$ for the entire range of variation in x. Consequently, measurements of the Soret coefficient with fairly large volumes at the column ends should best be performed with $y_e^* \omega_e < 0$, which is always possible by taking samples for analysis from the upper or lower vessel, the choice being determined by the one in which the concentration of the target component is reduced.

It is important that agreement between (18) and (24) is obtained over a wide range in x, since it enables us to increase the run time, and this is necessary when the mixture has a small Soret coefficient and the concentration shifts cannot be measured with sufficient precision in small times.

NOTATION

c, concentration; Δc, concentration change, τ, time; $\theta = H^2\tau/mK$, $H = g\rho^2\beta\delta^3(\Delta T)^2Bs/6!\eta$, $K = g^2\rho^3\beta^2\delta^7 \cdot (\Delta T)^2B/9!\eta^2D$, $m = \rho B\delta$; B, perimeter of separating slot; δ, gap; ΔT, temperature difference between hot and cold surfaces; s, Soret coefficient; $y = Hz/K$; z, vertical coordinate; $\omega = M/mL$; M, mass of mixture in tank; L, working length of a column. Indices: e, i, positive and negative ends of a column; 0, initial value.

LITERATURE CITED

1. G. D. Rabinovich, Inzh.-Fiz. Zh., 26, No. 3 (1974).
2. G. D. Rabinovich and M. A. Bukhtilova, Inzh.-Fiz. Zh., 26, No. 4 (1974).
3. G. D. Rabinovich, R. Ya. Gurevich, and G. B. Bobrova, Separation of Liquid Mixtures by Thermal Diffusion [in Russian], Nauka i Tekhnika, Minsk (1971).
4. C. Jones and V. Ferry, Isotope Separation by Thermal Diffusion [Russian translation], IL, Moscow (1971).
5. E. von Halle, AEC Research and Development Report, K-1420 (1959).

MODEL OF DIFFUSION TAKING INTO ACCOUNT SORPTION

V. I. Maron

UDC 533.73

The problem of the diffusion of a material in an adsorbing porous medium is considered. In the equation for the concentrations in the porous medium and the sorption layer a delay time is introduced.

The problem of the diffusion of material in an adsorbing porous medium is considered. Henry's law is assumed to hold for equilibrium values of concentration in the porous medium and in the sorption layer. This problem is considered, in a linear formulation, in a number of works where the kinetics of the process and diffusional transfer are taken into account; a review of such works appears in [1, 2].

The formulation of the problem outlined in the present paper differs from previous accounts in that a delay time is introduced in the equation relating the concentrations of the material in the porous medium and in the sorption layer.

If the concentration of the material in the sorbent layer is assumed to attain its equilibrium value at once, then Henry's law implies that its distribution will follow the distribution of the material in the porous medium. It is more general to assume that the distribution of material in the layer follows the distribution in the porous medium with some delay. The basis for this assumption is given in [3].

We introduce a delay time τ, assumed to be identical at all points of space. We denote the concentration of material in the flow by $\Theta(t, x)$ and the concentration in the sorption layer, by $a(t, x)$. On the basis of the given assumptions, the following relation exists between these functions:

$$a(t, x) = \Gamma\Theta(t-\tau, x),\ t \geqslant \tau,\ a \equiv 0,\ t < \tau. \tag{1}$$

Thus, the function $a(t, x)$ defined by Eq. (1) vanishes for $t < \tau$, and reaches its equilibrium value corresponding to the concentration of the material $\Theta(t, x)$ not at once, but τ units of the argument t later.

We shall show that for small values of the delay time τ, Eq. (1) gives the kinetic equation. To this end, we expand the function $\Theta(t - \tau, x)$ in a Taylor series in t:

$$\Theta(t-\tau, x) = \Theta(t, x) - \left(\frac{\partial\Theta}{\partial t}\right)_{\tau=0}\tau + \ldots. \tag{2}$$

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 3, pp. 453-455, March, 1976. Original article submitted July 29, 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $7.50.