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Application of *h*-Transformation for the Solution of Multicomponent Adsorption in Fixed Bed

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A procedure for the application of the so-called h-transformation in solving fixed-bed multicomponent adsorption problems is developed. In order to apply this procedure, it is necessary to select an appropriate value for the transition-motion factor ξ, and the criteria for making this selection are established in this work.

SCOPE

In studying sorptive processes in fixed beds, the assumption of local equilibrium between the fluid and sorbent phases is often invoked. With the use of this assumption, the mass transfer effect is eliminated. The concentration profile throughout the fixed bed can be predicted on the basis of stoichiometry and equilibrium relationship, which in most cases would be of sufficient accuracy for preliminary design and feasibility studies. Thus, important information about column behavior can be obtained without excessive calculation. The appeal of this approach is particularly strong when the fluid stream contains a number of species which interact and compete in the sorption process.

Although a number of investigators have considered the fixed-bed adsorption under equilibrium conditions (Wilson, 1940; DeVault, 1943; Walter, 1945; Glueckauf, 1946), the applicability of these results is rather restricted. In the present paper we demonstrate that the h-transformation proposed by Helfferich and Klein (1970) can be adapted to the nonstoichiometric system. The procedure established is different from that suggested by previous investigators (Klein et al., 1965, 1967; Vermeulen et al., 1973; Helfferich and Klein, 1970; Tondeur et al., 1965, 1967), and its use is demonstrated through an example problem.

CONCLUSIONS AND SIGNIFICANCE

Through an example problem and an examination of the mathematical expressions, a consistent procedure for applying the h-transformation to obtain the equilibrium solution of adsorption in fixed bed is developed. By extending the definition of the column capacity parameters T of the single component theory to multicomponent systems, the concentration profiles (or histories) can be obtained in the form of dimensionless concentration vs. $1/T$, provided a properly selected value of the transformation factor ξ is used in the H-function of the h-transformation. The results of the present work indicate that there is a unique correspondence between the adsorption and its equivalent stoichiometric system corresponding to this particular value of the transformation factor ξ. A criterion was established empirically for the selection of the transformation factor for cases where the adsorbents are initially free of any adsorbates. In more general cases, it is suggested that the correct solution can be obtained by using arbitrary values of ξ with the transition bounds modified by material balance considerations.

PREVIOUS WORK

For the case of liquid phase adsorption, a number of equilibrium solutions are available in the literature. DeVault (1943) obtained the solution for single species and outlined a procedure for cases when more than one species is present. Walter (1945) later gave a solution for two-component adsorption with constant separation factors, but there was an error in his work.* Glueckauf (1946) presented a solution on the development of concentration bands from the effluent stream of a chromatographic column for systems with Langmuir adsorption isotherm. An analogous solution was later given by Sillen (1950) who presented the results in terms of normalized variables instead of the effluent volume and column height as independent variables.

For the general case involving more than two species of adsorbates, Wilson (1940) gave a solution based on a very restricted type of equilibrium relationship, and his solution is of rather limited use. In more recent years, a complete treatise on the dynamic behavior of sorption processes in column operation has been authored by Helfferich (1964, 1967, 1968, 1970). Helfferich introduced the so-called h-transformation which replaces the concentrations (c_i) $i = 1, \ldots, n$ of the actual system by a new set of variables (h_i) $i = 1, \ldots, n$ whose profiles in the form of h_i vs. $1/T$ (or T, the column capacity parameter, defined later) follow a simple pattern. This approach was further extended by Klein, Tondeur, and Vermeulen (1965, 1967), Tondeur et al. (1965, 1967), and Vermeulen et al. (1973). These ivestigators formulated specific rules, which determine the nature of transition of the concentration profiles, and obtained solutions for the case of three and four components with constant separation factors. The h-transformation and its extension by these authors was, however, developed for ion exchange process but can be adapted to adsorption by viewing the adsorption system as an equivalent stoichiometric ion exchange system. Specific procedures for extending the h-transformation to adsorption have also been formulated by Helfferich and Klein (1970).

The work reported in this paper is an outgrowth of the authors' attempt to apply the Helfferich-Klein h-transformation procedure for the solution of multicomponent adsorption in fixed bed. During this work it was found that the Helfferich-Klein procedure led to a multitude of solutions, which clearly is physically unacceptable. Subsequent studies revealed the reason for this lack of uniqueness, and a modification of the original Helfferich-Klein procedure is suggested herein. It is hoped that the reporting of these results at this time will help to promote interest in and focus attention on the use of the h-transformation for the solution of nonstoichiometric sorption processes, whose significance apparently has not been widely recognized by workers in the field.

THE ORIGINAL HELFFERICH-KLEIN PROCEDURE

The development of h-transformation and its application to sorptive processes in fixed beds is discussed elsewhere in great detail (Helfferich and Klein, 1970). We shall merely outline the procedure and its application to adsorption developed by these investigators as a basis of discussion.

The problem considered here can be stated as follows. An influent stream containing n species of solutes with given initial concentrations $(c_{i_{in}})$ $i = 1, 2, \ldots n$ passes through a column of adsorbents of specified degree of presaturation (q_{io}), $i = 1, 2, \ldots n$. The numbering of the components is in the descending order of their adsorption affinity, that is, $a_1 > a_2, \ldots > a_i \ldots > a_n$. The equilibrium relationship is assumed to be that of Langmuir type; that is

$$q_j = \frac{a_j c_j}{1 + \sum_{i=1}^{n} b_i c_i} \quad j = 1, 2, \ldots, n \tag{1}$$

One is interested in obtaining the complete concentration profiles as functions of the column volume and the cumulative volume of the effluent under the condition of local equilibrium. The Helfferich-Klein procedure can be stated as follows.

1. Conversion of the adsorption system into an equivalent stoichiometric ion exchange system. In order to view the adsorption process as an equivalent ion exchange process, a fictitious component has to be introduced. Accordingly, an n-component adsorption system has an $(n + 1)$-component equivalent ion exchange system. The mole fraction of the equivalent ion exchange system in the fluid and solid phase, x_i and y_i, are given as

$$x_i = c_i \frac{b_i \xi}{a_i - \xi} \quad i = 1, 2, 3, \ldots, n \tag{2a}$$

$$y_i = q_i \frac{b_i}{a_i - \xi} \quad i = 1, 2, 3, \ldots, n \tag{2b}$$

For the fictitious component in the fluid and solid phases

$$x_{n+1} = 1 - \sum_{i=1}^{n} x_i \tag{3a}$$

$$y_{n+1} = 1 - \sum_{i=1}^{n} y_i \tag{3b}$$

In Equations (2a) and (2b), ξ is the transformation factor which, according to Helfferich and Klein, can be fixed arbitrarily because there is an infinite multitude of equivalent stoichiometric systems for every Langmuir system (see p. 286, Helfferich and Klein, 1970).

The fluid and solid phase concentrations (mole fraction) are related by the expression

$$\frac{y_j}{x_j} = \frac{1}{\sum_{i=1}^{n} \alpha_{ij} x_i} \tag{4}$$

where α_{ij}, the separation factor of $i - j$ component pair, is given as

$$\alpha_{ij} = \frac{a_i}{a_j} \quad i = 1, 2, \ldots, n \tag{5}$$

and

$$\alpha_{i,n+1} = \frac{a_i}{\xi} \tag{6}$$

2. Solution of the H-function. The h-transformation is given as

$$\sum_{i=1}^{n+1} \frac{x_i}{h - \alpha_{1i}} = 0 \tag{7a}$$

or in its alternative form as

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* Walter's error arises from his assumption that for the species with lower adsorption affinity (designated as species 2), the dimensionless concentration in the adsorbed phase $q_2/(q_{10} + q_{20})$, where q_{10} and q_{20} are the equilibrium concentrations of species 1 and 2 with respect to the influent, cannot exceed unity. This ignores the possibility of desorption of species 2, resulting from the competitive action between the species.

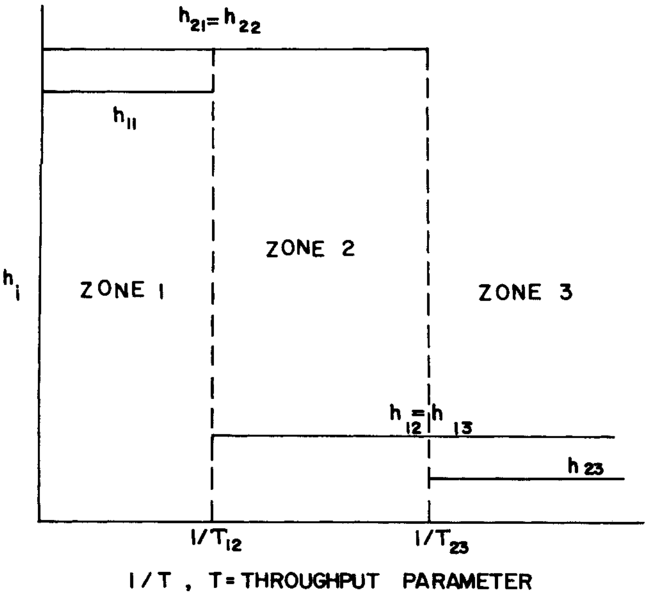

Fig. 1. *h*-Profile of a binary system.

$$\sum_{i=1}^{n+1} x_i \prod_{\substack{j=1\\ \neq i}}^{n+1} (h - a_{1j}) = 0 \tag{7b}$$

Accordingly, if the mole fractions of the equivalent ion exchange system are known, the corresponding h_i's can be found from the solution of the polynomial expression given above. As shown in the original development, Equation (7*b*) is a polynomial of the n^{th} power and has n real roots which are designated as $h_1, h_2, \ldots, h_n$ in the ascending order of their magnitude. Accordingly, there is no corresponding value of h for the fictitious species, but there is one-to-one correspondence between c_i and h_i for all the species present in the adsorption system.

3. Determination of the *h*-profiles. Similar to the concentration profile, the *h*-profile in the form of h_i vs. $1/T$, with the column capacity parameter T defined by

$$T = \frac{(V - \epsilon v) \sum_{i=1}^{n} c_{i\,in}}{v\rho \sum_{i=1}^{n} (q_{i\,in})} \tag{8}$$

consists of $(n + 1)$ zones (plateau regions) for an n-component adsorption system, over each of which the values of h_i's remain constant. Changes in values of h_i's take place between plateaus, which can be either gradual or abrupt. However, for adsorption systems obeying Langmuir adsorption isotherm [Equation (1)], the change is always abrupt.

The advantage of using *h*-profile over that of *c*-profile is its simplicity and orderliness. If one uses a double subscript notation* with the first subscript denoting species and the second plateau regions for the k^{th} species of the n-component adsorption system we get

$$h_{k1} = h_{k2} = h_{k3} = \ldots = h_{k\,k} \tag{9a}$$

$$h_{k\,k+1} = h_{k\,k+2} = \ldots\ \ldots = h_{k\,n+1} \tag{9b}$$

Namely, there is only one change in value in the *h*-profile for any given species. Thus, it is possible to determine the complete set of *h*-profiles if the influent concentrations and initial concentrations of the adsorbents in the column are known. The first plateau zone of the h_i vs. $1/T$ curve corresponds to the influent conditions (namely, small $1/T$, small bed volume, large effluent volume, or time). The last plateau zone corresponds to that of the initial state of the absorbent. In terms of double subscript notation, one has

$$c_{i\,in} = c_{i1} \tag{10a}$$

$$i = 1, 2, \ldots, n$$

$$q_{i_o} = q_{i\,n+1} \tag{10b}$$

The corresponding values of q and c (that is, q_{i1} and $c_{i\,n+1}$) can be found from the equilibrium relationship [that is, Equation (1)].

The nature of the change of the value of h_k over the h_k vs. $1/T$ profile is determined by the value of the parameter $\overline{R}_{k,k+1}$, defined as

$$\overline{R}_{k,k+1} = \frac{h_{k\,n+1}}{h_{k1}} \tag{11}$$

The change of h_k over the plateau regions k and $(k + 1)$ is abrupt if $\overline{R}_{k,k+1} < 1$ and gradual if $\overline{R}_{k,k+1} > 1$. As stated earlier, for systems obeying Langmuir adsorption isotherm, the change is always abrupt. The values of T at which this change takes place (transition bound) are given by

$$\overline{T}_{k\,k+1} = (h_{k\,k+1}\, h_{k1}\, P_k)^{-1} \tag{12}$$

$$P_k = \prod_{\substack{i=1\\ \neq k}}^{n} h_{ik} \prod_{i=1}^{n+1} \alpha_{1i} \tag{13}$$

A schematic diagram of the *h*-profile is shown in Figure 1.

4. Conversion of the *h*-profiles into the concentration profiles. Once the *h*-profiles are known, they can be converted easily into the concentrations (mole fractions) of the equivalent stoichiometric system by using the following relationships:

$$x_{jk} = \frac{\prod_{i=1}^{n} (h_{ik} - \alpha_{1j})}{\prod_{\substack{i=1\\ \neq j}}^{n+1} (\alpha_{1i} - \alpha_{1j})} \tag{14a}$$

$$j = 1, 2, \ldots, n + 1$$

$$k = 1, 2, \ldots, n + 1$$

$$y_{jk} = \frac{\prod_{i=1}^{n} [(1/h_{ik}) - \alpha_{j1}]}{\prod_{\substack{i=1\\ \neq j}}^{n+1} (\alpha_{i1} - \alpha_{j1})} \tag{14b}$$

From these, the concentrations of the adsorption system can be obtained as

$$c_i = x_i \frac{a_i - \xi}{b_i \xi} \tag{15}$$

$$q_i = y_i \frac{a_i - \xi}{b_i} \tag{16}$$

In general, the procedure outlined above is simple and

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* For the sake of convenience, the single subscript will be used wherever there is no ambiguity. The single subscript always refers to species.

straightforward. The only tedious step is that of the solution of the polynomial to obtain values of h_i [Equation (7*b*)]. However, this can be handled without difficulty unless the value of n is exceedingly large.

AN EXAMPLE

To test the procedure outlined above, an example problem is presented here. Consider the adsorption of aqueous solution of phenol and Conoco C-550 (a commercial grade of alkyl benzene sulfonate manufactured by the Continental Oil Company) in a column of fresh activated carbon. This example is selected because of its simplicity and the fact that the two-component adsorption problem has been solved previously by Glueckauf, providing a basis of comparison.

The equilibrium relationship for the system activated carbon—aqueous solution of phenol and Conoco C-550 has been determined by Hsieh (1974) and found to obey the Langmuir type of adsorption isotherm. With phenol designated as species 1 and Conoco C-550 as 2, the adsorption isotherms are

$$q_1(\text{in } \mu\text{-mole/cm}^3) = \frac{(310)\ (2.5)\ c_1}{1 + 2.5\,c_1 + 0.056\,c_2}$$

$$q_2(\text{in } \mu\text{-mole/cm}^3) = \frac{(970)\ (0.056)\ c_2}{1 + 2.5\,c_1 + 0.056\,c_2}$$

or

$$a_1 = (310)\ (2.5) \qquad b_1 = 2.5$$

$$a_2 = (970)\ (0.056) \qquad b_2 = 0.056$$

If the transformation factor ξ is chosen to be unity, the separation factors are

$$\alpha_{11} = 1$$

$$\alpha_{12} = (310)\ (2.5)/(970)\ (0.056) = 14.2673$$

$$\alpha_{13} = \frac{a_1}{\xi} = (310)\ (2.5) = 775$$

For this two-component adsorption system, the equivalent stoichiometric ion exchange system is a ternary one. The h-profile covers three plateau regions. The mole fractions of the equivalent stoichiometric system corresponding to the inlet conditions (x_{i1} and y_{i1}, $i = 1, 2, 3$) are found from Equations (2*a*), (2*b*), (3*a*), and (3*b*):

$$x_{11} = 0.1615 \qquad x_{21} = 0.31508 \qquad x_{31} = 0.52342$$

$$y_{11} = 0.87648 \qquad y_{21} = 0.11985 \qquad y_{31} = 0.00367$$

The mole fractions corresponding to the initial column condition (x_{i3} and y_{i3}, $i = 1, 2, 3$) are

$$y_{13} = 0 \qquad x_{13} = 0$$

$$y_{23} = 0 \qquad x_{23} = 0$$

$$y_{33} = 1 \qquad x_{33} = 1$$

The h's for the first and third plateau are as follows.

For the first plateau. From Equation (7*b*) and the values of x_{i1}, one has $0.615\ (h\text{-}14.2673)\ (h\text{-}775) + 0.31508\ (h - 1)\ (\text{-}775) + 0.52342\ (h - 1)\ (h\text{-}14.2673) = 0$. The roots of this quadratic equation are

$$h_{11} = 5.43998 \qquad h_{21} = 374.51805$$

For the third plateau. One has

$$(1)\ (h - 1)\ (h\text{-}14.2673) = 0$$

and

$$h_{13} = 1 \qquad h_{23} = 14.2673$$

Table 1. *h*-Profiles of the Example Problem with Arbitrary Values of ξ

Species \ Zone	1	2	3
1	5.43998	1.0	1.0
2	374.51805	374.51805	1.0

ξ \ Transition bounds	$1/T_{12}$	$1/T_{23}$
1	0.18426	0.48325
10	1.84268	4.83249
54	9.94994	26.09545

Table 2. Concentration Profile of the Example Problem with Arbitrary Values of ξ

	Liquid phase concentration (μ-ml/m^3)		
Species \ Zone	1	2	3
1	50	0	0
2	300	450.8946	0

Transition bounds same as Table 1

The parameters $R_{k,k+1}$ are

$$\overline{R}_{1.2} = \frac{k_{13}}{k_{11}} = \frac{1}{5.43968} < 1 \quad \overline{R_{2.3}} = \frac{k_{23}}{k_{21}} = \frac{14.2673}{374.51805} < 1$$

Therefore, both transitions are abrupt. The transition bounds are calculated from Equations (12) and (13). From $\overline{T}_{12}$, one has

$$\overline{T}_{12} = (h_{13}\,h_{11}\,P_1)^{-1}$$

$$P_1 = h_{21}(\alpha_{11}\,\alpha_{21}\,\alpha_{31})$$

$$= (374.51805)\ (1) \left(\frac{1}{14.2673}\right) \left(\frac{1}{775}\right) = 0.033871$$

$$\overline{T}_{12} = (5.34998 \cdot 0.033871)^{-1} = 5.42717$$

$$\text{and} \quad 1/\overline{T}_{12} = 0.18426$$

The h-profile, therefore, can be constructed as shown in Table 1. The same calculations were repeated by choosing $\xi = 10$ and $\xi = 54$. The results are also given in Table 1. It is evident that one obtains different h-profiles for different values of ξ chosen. The differences are in the transition bounds but not in the values of h_I's. Identical results were obtained by using the modified version of the h-transform of Klein et al. (1967). The concentration profiles in the form of c_i vs. $1/T$ can be readily obtained from the h-profile by using Equations (14*a*) to (15). These results are presented in Table 2.

The fact that one can obtain a multitude of solutions depending upon the value of the transformation factor ξ clearly suggests the need for clarification. In the following sections the reason for the occurrence of the multiple solutions is examined, and a procedure is proposed in order to obtain the correct solutions.

MODIFICATION OF THE HELFFERICH-KLEIN PROCEDURE

The example given above indicates that the values of h's of the various plateau regions of the h_i vs. $1/T$ profile remain constant regardless of the values of ξ chosen. But the transition bound varies with ξ. In fact, there is an inverse proportionality between the transition bound and the value of ξ used as shown in the example below:

For $1/T_{12}$, 0.18426: 1.8426: 9.94794 = 1: 10: 54

For $1/T_{23}$, 0.483249: 4.87249: 26.09545 = 1: 10: 54

The reason for this behavior can be seen directly from the procedure suggested. The values of h's are given by Equation (7*b*). In its expanded form, this is given as

$$\begin{aligned} & x_1(h-\alpha_{12})(h-\alpha_{13})\cdots(h-\alpha_{1\,n+1}) \\ & \quad + (h-\alpha_{11})\,x_2(h-\alpha_{13})\cdots(h-\alpha_{1\,n+1}) + \cdots \\ & \quad + (h-\alpha_{11})(h-\alpha_{12})\cdots(h-\alpha_{1\,n-1})\,x_n(h-\alpha_{1\,n+1}) \\ & \quad + (h-\alpha_{11})(h-\alpha_{12})\cdots(h-\alpha_{1n})\,x_{n+1} = 0 \end{aligned}$$

Since $x_{n+1} = 1 - (x_1 + x_2 + \cdots x_n)$, the above expression can be written as

$$\begin{aligned} & \prod_{i=1}^{n}(h-\alpha_{1i}) + \sum_{i=1}^{n} x_i \left[\prod_{\substack{j=1\\ \neq i}}^{n}(h-\alpha_{1j})\right][(h-\alpha_{1\,n+1}) \\ & \quad - (h-\alpha_{1i})] = \prod_{i=1}^{n}(h-\alpha_{1i}) \\ & \quad + \sum_{i=1}^{n}\alpha_{1i}\,x_i\left[\prod_{\substack{j=1\\ \neq i}}^{n}(h-\alpha_{1j})\right]\left(1-\frac{\alpha_{1\,n+1}}{\alpha_{1i}}\right) \\ & = \prod_{i=1}^{n}(h-\alpha_{1i}) + \sum_{i=1}^{n}\alpha_{1i}(1-\alpha_{i\,n+1}) \\ & \qquad x_i\left[\prod_{\substack{j=1\\ \neq i}}^{n}(h-\alpha_{1j})\right] = 0 \end{aligned}$$

since

$$\alpha_{i,n+1} = \frac{\alpha_{1\,n+1}}{\alpha_{1i}}$$

The quantity $(1 - \alpha_{i\,n+1})\,x_i$ appearing in the second series of the above expression, when written in terms of the quantities of the original adsorption system and the transformation factor [that is, Equations (2*a*) and (6)], becomes

$$\begin{aligned} (1-\alpha_{i\,n+1})\,x_i &= c_i\frac{b_i\,\xi}{a_i-\xi}\left(1-\frac{a_i}{\xi}\right) \\ &= c_i\frac{b_i\,\xi}{a_i-\xi}\,\frac{\xi-a_i}{\xi} = -\,b_ic_i \end{aligned}$$

Accordingly, the equation from which the values of h's are obtained is given as

$$\prod_{i=1}^{n}(h-\alpha_{1i}) - \sum_{i=1}^{n}\alpha_{1i}b_ic_i\left[\prod_{\substack{j=1\\ \neq i}}^{n}(h-\alpha_{1j})\right] = 0 \tag{17}$$

In other words, h_i's are dependent upon the liquid-phase concentration as well as adsorption isotherm parameters (note that the separation factor involving the fictitious component does not appear in the above expression) and are independent of the transformation parameter chosen as demonstrated previously in the example calculation.

TABLE 3. CORRECT SOLUTION OF THE EXAMPLE PROBLEM

Species \ Zone	Liquid phase concentration (μ-mole/m^3)		
	1	2	3
1	50	0	0
2	300	450.8948	0

Transition bounds: $1/T_{12} = 0.20293$
$1/T_{23} = 0.53223$

Similarly, one can show that the conversion of h_i's into c_i's are also independent ot ξ. By Equation (14*a*) to (15)

$$\begin{aligned} c_{jk} &= x_{jk}\frac{a_j-\xi}{b_j\xi} \\ &= \frac{\displaystyle\prod_{i=1}^{n}(h_{ik}-\alpha_{1j})}{\displaystyle\prod_{\substack{i=1\\ \neq j}}^{n}(\alpha_{1i}-\alpha_{1j})}\left(\frac{1}{\alpha_{1\,n+1}-\alpha_{1j}}\right)\frac{a_j-\xi}{b_j\xi} \end{aligned} \tag{18}$$

since

$$\begin{aligned} \frac{1}{\alpha_{i\,n+1}-\alpha_{1j}}\,\frac{a_j-\xi}{b_j\xi} &= \frac{1}{\alpha_{1j}}\,\frac{a_j-\xi}{b_j\xi}\,\frac{1}{\dfrac{\alpha_{1\,n+1}}{\alpha_{1j}}-1} \\ &= \frac{1}{\alpha_{1j}}\,\frac{a_j-\xi}{b_j\xi}\,\frac{1}{{\alpha_{j\,n+1}}^{-1}} = \frac{1}{\alpha_{1j}\,b_j} \end{aligned}$$

or

$$c_{jk} = \frac{\displaystyle\prod_{i=1}^{n}(h_{ik}-\alpha_{1j})}{\displaystyle\prod_{\substack{i=1\\ \neq j}}^{n}(\alpha_{1i}-\alpha_{1j})}\,\frac{1}{\alpha_{1j}\,b_j} \tag{19}$$

namely, the calculation of c_j from the h_i's does not involve ξ, or quantities dependent upon ξ.

The relationship between the transition bounds and ξ can be seen easily from Equations (12) and (13). Since the h_i's are independent of ξ, while P_k is proportional to ξ, we have

$$\overline{T}_{k\,k+1} \propto (\xi)^{-1} \quad \text{or} \quad 1/\overline{T}_{k\,k+1} \propto \xi$$

which is what was observed in the example. Although Equations (2*a*) and (2*b*) suggest the existence of a multiple equivalent stoichiometric ion exchange system for each adsorption system, in reality there is a unique correspondence between the stoichiometric and adsorption systems corresponding to a particular value of ξ with the column capacity parameter defined by Equation (8). The criteria for the selection of the transformation factor are presented below.

The correct answer for this particular example can be obtained from the solution of Glueckauf (1947). The h_i's concentration profiles are shown in Table 3, which differ from all three solutions obtained earlier. Since it has been shown that the transition bound is inversely proportional to the value of ξ used in calculations, the correct value of the transformation factor is found to be

$$(\xi)_{\text{correct}} = \frac{(1/T)_{\text{Glueckauf}}}{(1/T)_{\xi=1}} = \frac{0.20293}{0.104258} = 1.10136$$

TABLE 4. EVALUATION OF CORRECT ξ VALUES FOR THE EXAMPLE PROBLEMS WITH DIFFERENT INLET CONDITIONS

c_{11}	c_{21}	q_{11}	q_{21}	c_{22}	q_{22}	ξ_{correct}
50	300	271.35854	114.11765	450.89448	933.04775	1.10136
25	150	269.47149	113.32406	222.79995	898.02444	2.18740
10	60	263.96458	111.00817	86.23806	803.60013	5.35675
5	30	255.27009	107.35178	41.14670	676.43558	10.36036
3	18	244.53092	102.83551	23.50045	551.17901	16.54126
1.5	9	221.25999	93.04911	10.85537	366.72899	29.93420
1.4	8.4	218.29229	91.80106	10.05183	349.35994	31.64218
1.3	7.8	214.96544	90.40198	9.25586	331.13931	33.55686
1.2	7.2	211.21003	88.82267	8.46812	312.02261	35.71818
1	6	202.03337	84.96350	6.92044	270.92344	40.99955
0.8	4.8	189.67205	79.76505	5.41561	225.72078	48.11377
0.7	4.2	181.72987	76.42503	4.68172	201.48611	52.68467
50	250	276.78571	97.00000	400.21886	928.56871	1.24595
50	50	300.85404	21.08696	194.12314	888.28755	3.21941
50	40	302.16781	16.94323	183.46648	883.96226	3.54568
50	20	304.83008	8.54626	161.89745	873.63846	4.47681
50	10	306.17889	4.29204	150.94618	867.38692	5.17452
100	300	289.39507	60.85138	604.53813	942.16973	0.87562
200	300	299.34338	31.47161	914.64746	951.42483	0.66163
300	300	302.81323	21.22428	1226.16694	956.07629	0.54006
400	300	304.57850	16.01100	1538.24591	958.86871	0.45799
500	300	305.64758	12.85376	1850.60251	960.72957	0.39813

To establish empirically a criterion for selecting ξ, a large number of calculations were made for the same system as the example problem but with different inlet conditions. The correct answers were obtained by using Glueckauf's solution. The transition bounds were also calculated by using the Helfferich-Klein procedure assuming $\xi = 1$. The correct values of ξ were obtained by taking the ratio of $(1/T)_{\text{Glueckauf}}$ and $(1/T)$. These results are summarized in Table 4.

By trial and error it was found that the correct value of ξ for all the cases in Table 4 is given by

$$\xi = \frac{q_{11} + q_{21}}{c_{11} + c_{21}} \tag{20}$$

For an n-component fluid stream passing through a bed of fresh adsorbent, based on intuitive reasoning, one would expect

$$\xi = \frac{\prod_{i=1}^{n} q_{i1}}{\prod_{i=1}^{n} c_{i1}} \tag{21}$$

While we have not been able to obtain a rigorous proof for the above expression, the validity of this expression can be argued on physical grounds. The transformation factor ξ, according to Klein et al. (1967), can be considered to be given by

$$\xi = \frac{q_{i,\text{ref}}}{c_{i,\text{ref}}} \tag{22}$$

where $q_{i,\text{ref}}$ and $c_{i,\text{ref}}$ are the scaling factors converting the concentration of the adsorption system into the mole fractions of the equivalent stoichiometric ion exchange system, or

$$x_i = \frac{c_i}{c_{i,\text{ref}}} \tag{23a}$$

$$y_i = \frac{q_i}{q_{i,\text{ref}}} \tag{23b}$$

One can, therefore, consider ξ as the ratio of the total concentration of all species present in the absorbent phase of the equivalent stoichiometric system to that of the liquid phase. For the adsorption problem in a column consisting of fresh adsorbent, one can assume that there is no fictitious component present in the influent, and

$$c_{i,\text{ref}} = \sum_{i=1}^{n} c_{i1} \tag{24}$$

Similarly, to determine the value of $q_{i,\text{ref}}$, consider the situation when the bed becomes saturated with the influent. For the equivalent ion exchange system, this corresponds to the complete exhaustion of the fictitious species originally present in the adsorbent phase. Accordingly

$$q_{i,\text{ref}} = \sum_{i=1}^{n} q_{i1} \tag{25}$$

which leads to the condition stated before. This condition, however, only holds true for beds initially free of adsorbent and is not applicable when the adsorbents of the column are partially saturated initially with some or all of the species of adsorbates.

A more direct approach utilizes a material balance. For the example examined above, if one considers the overall balance for species 1 from time zero to complete saturation, for a column of volume v and porosity ϵ, one has

$$v\rho q_{11} + v\epsilon \cdot c_{11} = \int_0^{\infty} (c_{1_{\text{in}}} - c_{1_{\text{out}}}) \cdot dV \tag{26}$$

where the subscripts in and out refer to the influent and effluent conditions, and $c_{i_{\text{in}}} = c_{11}$,

For the concentration profile established previously, one has*

$$c_{1_{\text{out}}} = 0 \qquad V < V_{\text{tran}}$$

$$c_{1_{\text{out}}} = c_{11} \qquad V > V_{\text{tran}}$$

and V_{tran} is related to T_{12} according to its definition, or

$$T_{12} = \frac{(V_{\text{tran}} - v\epsilon)(c_{11} + c_{21})}{v\rho(q_{11} + q_{21})}$$

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* As shown in the example discussed above, the Helfferich-Klein procedure, while incapable of predicting the correct transition bound, gives correct values of the concentration.

The material balance yields

$$v\rho q_{11} + v\epsilon c_{11} = V_{\text{tran}} c_{11} \tag{27}$$

or

$$\frac{(V_{\text{tran}} - v\epsilon)c_{11}}{v\rho q_{11}} = 1$$

and

$$T_{12} = \frac{q_{11}}{c_{11}} \frac{(c_{11} + c_{21})}{(q_{11} + q_{12})} \tag{28}$$

Accordingly, if one carries out the calculation by using an arbitrary value of $\xi = \xi_o$ and obtains the appropriate transition bounds $(T_{k,k+1})_{\xi_o}$, then transition bound values can be easily corrected once the correct value of any bound is known since $1/T_{k,k+1}$ is shown to be proportional to the value of ξ used. For the present case, the correct value shall be

$$(1/T_{k,k+1}) = (1/T_{k,k+1})_{\xi_o} \cdot \frac{(1/T_{12})}{(1/T_{12})_{\xi_o}}$$

If these results are applied to the example, it is found to be

$$1/T_{12} = 0.20293$$

In the example discussed above with $\xi = 1$, the calculation yields

$$1/T_{12} = 0.18426$$

$$1/T_{23} = 0.48325$$

The correct value of $1/T_{23}$ is, therefore

$$(1/T_{23})_{\text{correct}} = (1/T_{23})_{\xi=1} \frac{0.20293}{0.18426} = 0.53223$$

Alternatively, the material balance can be made for the second species. The appropriate equation is

$$v\rho q_{21} + v\epsilon c_{21} = \int_0^\infty (c_{2\text{in}} - c_{2\text{out}}) \cdot dV \tag{29}$$

$$c_{2\text{in}} = c_{21}$$

$$c_{2\text{out}} = 0 \qquad V < V_{\text{tran}_1}$$

$$c_{2\text{out}} = c_{22} \qquad V_{\text{tran}_1} < V < V_{\text{tran}_2}$$

$$c_{2\text{out}} = c_{21} \qquad V > V_{\text{tran}_2}$$

where V_{tran_1} and V_{tran_2} correspond to the transition bound value $1/T_{23}$ and $1/T_{12}$, respectively. The above expression can be rewritten to yield

$$\begin{aligned} v\rho q_{21} + v\epsilon c_{21} &= c_{21}V_{\text{tran}_1} + (c_{21} - c_{22})(V_{\text{tran}_2} - V_{\text{tran}_1}) \\ &= c_{21}V_{\text{tran}_2} - c_{22}V_{\text{tran}_2} + c_{22}V_{\text{tran}_1} \end{aligned}$$

and

$$\begin{aligned} v\rho q_{21} = c_{21}[V_{\text{tran}_2} - \epsilon v] - c_{22}[(V_{\text{tran}_2} - \epsilon v) \\ - (V_{\text{tran}_1} - \epsilon v)] = \frac{q_{11} + q_{21}}{c_{11} + c_{21}} T_{23}\left[\frac{c_{21}}{q_{21}} \frac{T_{12}}{T_{23}} \right. \\ \left. - \frac{c_{22}}{q_{21}} \left(\frac{T_{12}}{T_{23}} - 1 \right) \right] \end{aligned}$$

Since the ratio of the transition bounds is independent of the value of ξ used, the value of T_{12}/T_{23} can be obtained from the calculation made for $\xi = 1$, that is, $T_{12}/T_{23} = 0.48325/1.18426 = 2.6227$. Together with the concentration values, T_{23} is found to be:

$$1/T_{23} = 0.5223$$

which is the same as the value of T_{23} based on the material balance of species 1.

The advantage of using this corrected procedure lies in its simplicity and generality. The same principle can be easily applied to cases where the adsorbents are partially saturated with some or all the species. This is confirmed through numerous sample calculations.

From the above discussion and example, a consistent procedure for applying the Helfferich-Klein *h*-transformation to adsorption calculations is developed. For cases where the adsorbents are initially free of any adsorbate, the selection of the transformation factor is given by Equations (21). Alternatively, one may make the calculation by using arbitrary values of ξ and then correcting the transition bounds through material balance considerations. This latter approach is preferred because of its generality and its applicability to fresh as well as partially saturated adsorbents.

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NOTATION

a_i = Langmuir isotherm parameter of component *i*, Equation (1)
b_i = Langmuir isotherm parameter of component *i*, Equation (1)
c_i = concentration of component *i* in fluid phase
h_i = *h* variable of component *i*, defined by Equation (7*a*) or (7*b*)
P_k = parameter defined by Equation (13)
q_i = concentration of component *i* in adsorbed phase
$R_{k,k+1}$ = criteria for transition nature, Equation (11)
T = column capacity parameter defined by Equation (8)
V = volume of fluid passing through the column
v = volume of column
x_i = mole fraction of component *i* of the equivalent stoichiometric ion exchange system
y_i = mole fraction of component *i* of the equivalent stoichiometric ion exchange system

Greek Letters

α_{ij} = separation factor of pair *i-j* defined by Equation (5)
$\alpha_{i,n+1}$ = separation factor of component *i* with respect to the fictitious component $[(n + 1)^{\text{th}}]$ of the equivalent stoichiometric system, Equation (6)
ϵ = porosity of bed
ρ = bulk density of adsorbent
ξ = transformation factor

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An Effective Computational Algorithm for Suboptimal Singular and/or Bang-Bang Control

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I. Theoretical Developments and Applications to Linear Lumped Systems

A new and simple computational algorithm for obtaining suboptimal singular and/or bang-bang solutions of typical lumped and distributed parameter control problems is proposed. The algorithm is based on the piecewise maximization of the Hamiltonian and a limiting process utilizing a penalty function of the control variables. Theoretical developments and computational applications of the algorithm to several linear lumped parameter control problems are presented. Extensions and applications of the algorithm to nonlinear and distributed parameter systems are given in Part II.

SCOPE

The application of optimal control theory to dynamic systems of interest to the chemical process industry is often hampered by the existence of constraints, in addition to the common characteristics of these systems of having high state dimensionality, extreme nonlinearity, and multiple controls. The maximum principle formulation (Pontryagin et al., 1962) of such optimization problems leads to a nonlinear, two-point, boundary value problem which is difficult to solve numerically. Even though effective algorithms have been developed to calculate the optimal control policies for dynamic systems, the solution of many classes of optimization problems, especially those with nonlinear and distributed parameter characteristics, still requires excessive computation time and computer storage when these algorithms are applied. Suboptimal control is an attempt to approximate the solution to these problems with a reduced amount of computer storage and computation time. From a chemical engineering point of view, the use of suboptimal control is justified in many

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