**Binary Mixtures.** Multiplying out eq 17 gives

$$\delta G = \frac{1}{2}\{\mu_{11}^{I}\eta_1^2 + \mu_{11}^{II}(\eta_1 + (N_1^{I} - N_1^{II})\eta_2)^2\} \quad (21)$$

Since $\eta_1$ and $\eta_2$ are completely arbitrary, we see that $\delta G > 0$ if and only if $\mu_{11}^{I} > 0$ and $\mu_{11}^{II} > 0$. This agrees with the earlier result in eq 16.

**Ternary Mixtures.** Let us now suppose that we have found a local minimum in $G$ such that $\mathbf{G}^{I}$ is positive definite and $\mathbf{G}^{II}$ is indefinite. Consider the variation $\eta_1 = \eta_2 = 0$, $\eta_3 \neq 0$. Such a variation isolates the $\mathbf{G}^{II}$ matrix. Thus

$$\delta G = \frac{1}{2}\eta_3^2 \cdot [a, b] \begin{bmatrix} \mu_{11}^{II} & \mu_{12}^{II} \\ \mu_{21}^{II} & \mu_{22}^{II} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} \quad (22)$$

where we let $a = (N_1^{I} - N_1^{II})$, $b = (N_2^{I} - N_2^{II})$. By hypothesis, $\mathbf{G}^{II}$ is indefinite and $a$ and $b$ are either positive or negative constants. Under these conditions the quadratic form in eq 22 will not generally be greater than zero. This contradicts the original proposition that $\delta G > 0$ for all possible variations. Nevertheless, it is conceivable that the $\mu_{ij}^{II}$'s happen to have values which make this quadratic form positive for the particular values of $a$ and $b$ prevailing at the equilibrium point under examination. Therefore, Dr. Michelsen is correct when he says that it is possible to find a two-phase minimum in $G$ with one of the phases materially unstable. We do not think this is very likely, in general, and it presumably corresponds to a very special event on a ternary phase diagram. It certainly is not a commonplace event.

Finally, we will consider the case of an azeotropic equilibrium. For such equilibria, the molar Gibbs free energy of the liquid is equal to that of the vapor

$$g^{L} = \sum_{i=1}^{c} \mu_i^{L}x_i; \ g^{v} = \sum_{I=1}^{c} \mu_i^{v}y_i; \ \text{and} \ x_i = y_i \ (i = 1,2, ..., c); \ \mu_i^{L} = \mu_i^{v} \ (i = 1, 2, ..., c) \quad (23)$$

and hence the $G$ surface for the overall system displays a linear trough (as opposed to a banana shaped trough) with a horizontal bottom. This is precisely why det $\mathbf{H} = 0$ for azeotropic mixtures.

For such mixtures we show that $\delta G$ takes on a special form, namely

$$\delta G = \frac{1}{2}\alpha_1^{T}[\mathbf{G}^{I} + \mathbf{G}^{II}]\alpha_1 \quad (24)$$

This is even true for *binary* mixtures as can be verified by multiplying out the quadratic form in eq 10 above and then using the Gibbs–Duhem equations to get

$$\delta G = (\mu_{11}^{I} + \mu_{11}^{II}) \ (\epsilon_1 - N_1^{I}\epsilon_2)^2 \quad (25)$$

Hence, for azeotropic equilibria it is possible to locate a minimum in $G$ with one of the phases materially unstable. Moreover, this is a much more likely event that the corresponding situation for nonazeotropic mixtures. The reason for this is evident from the way $\mathbf{G}^{I}$ and $\mathbf{G}^{II}$ appear together in eq 24 but individually in eq 17.

More than all this, our paper not only develops the appropriate mathematics to discover this phenomenon, but it also gives an interpretation on a binary phase diagram. The spurious homogeneous azeotrope pin-pointed in Figure 18 in our paper is typical of the situation discussed above. At this point, $\mu_{11}^{L} < 0$; $\mu_{11}^{v} > 0$, and as we say in the paper, such an equilibrium is indeed spurious.

### Literature Cited

Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258–267.
Cahn, J. W. *Acta Metall.* **1961**, *9*, 795–801.
Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93–99.
Callen, H. B. "Thermodynamics"; Wiley: New York, 1960.
Derham, K. W.; Goldsbrough, J.; Gordon, M. *Pure Appl. Chem.* **1974**, *38*, 97–116.
Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1–32.
Kwei, T. K.; Wang, T. T. "Phase Separation Behavior of Polymer–Polymer Mixtures", in "Polymer Blends", Vol. I, Paul, D. R.; Newman, S., Ed.; Academic Press: New York, 1978.
Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568–2580.
Prigogine, I.; Defay, R. "Chemical Thermodynamics" (Translated by Everett, D. H.), Longmans: London, 1965.
Reid, R. C. *Chem. Eng. Educ.* **1978a**, Spring Issue, 60; **1978b**, Summer Issue, 108; **1978c**, Fall Issue, 194.
Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145–1156.
Sanchez, I. C. "Statistical Thermodynamics of Polymer Blends", Chapter 3 in "Polymer Blends", Vol. I, Paul, D. R.; Newman, S., Ed., Academic Press: New York, 1978.
Sanchez, I. C. *J. Macromol. Sci.-Phys.* **1980**, *B17*(3), 565–589.
Van Dongen, D. B.; Doherty, M. F.; Haight, J. R. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 472–485.

*Department of Chemical*      **Michael F. Doherty***
*Engineering*      **David B. Van Dongen**
*University of Massachusetts*      **James R. Haight**
*Amherst, Massachusetts 01003*

---

## Comments on "Effect of Vapor Efflux from a Spherical Particle on Heat Transfer from a Hot Gas"

*Sir:* In a recent paper Kalson (1983) concluded that the Ackermann factor

$$\Xi_H = \frac{\phi_H}{\exp(\phi_H) - 1} \quad (1)$$

for correction of the heat transfer from a solid body to a gas stream to account for finite rates of mass transfer, depends on the geometry of the body. He obtained significantly different results for the flat plate and spherical geometries. This apparent dependence of $\Xi_H$ on the geometry considered is more than a little disquieting and we show below that this is a direct consequence of his definition of the heat transfer coefficients in the two cases

$$h = k_H/\delta \quad (2)$$

where $\delta$ is the "film" thickness. It is the object of the present communication to show that if an alternative, more physically meaningful, definition of the heat transfer coefficient is employed, taking proper account of the curvature of the interface, and proper nondimensionalized parameters are used, identical values of the Ackermann correction factors are obtained for planar, cylindrical, and spherical geometries. The results are generalizable to the consideration of the effect of mass transfer on the *mass* transfer coefficients in nonideal multicomponent fluid mixtures, showing the general applicability of the form of the Ackermann correction factor, eq 1.

In view of our objective to generalize the Ackermann theory, we use a consistent nomenclature, different fro that adopted by Kalson (1983), and employ molar units in place of mass units. An entirely parallel treatment holds for mass units.

For steady-state transport in nonreacting mixtures, the equations of continuity of mass and energy reduce to

$$\frac{d(r^\nu N_{ir})}{dr} = 0 \quad (i = 1,2, ..., n); \quad \frac{d(r^\nu E_r)}{dr} = 0 \quad (3)$$

where $\nu = 0, 1$, and 2 respectively stand for planar, cylin-
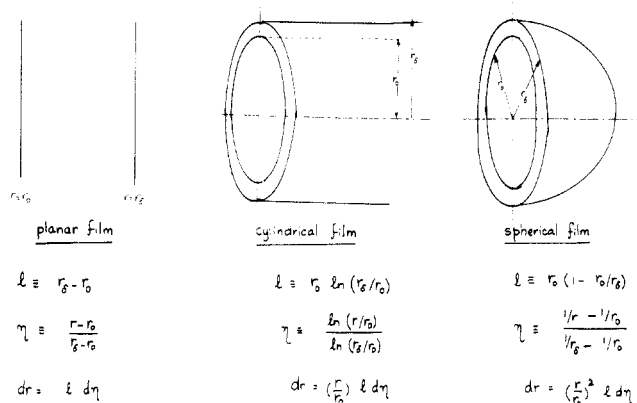
**Figure 1.** Definition of the characteristic length $l$ and dimensionless distance $\eta$ for planar, cylindrical, and spherical shaped bodies.

drical, and spherical geometries. If the transfer processes are confined to the region bounded by $r = r_0$ and $r = r_\delta$ (see Figure 1), then eq 3 gives

$$r^\nu N_{ir} = r_0{}^\nu N_{i0} = r_\delta{}^\nu N_{i\delta} \quad (i = 1,2, ..., n);$$
$$r^\nu E_r = r_0{}^\nu E_0 = r_\delta{}^\nu E_\delta \quad (4)$$

The energy flux $E_r$ is made up of the conductive and convective enthalpy contributions

$$E_r = q_r + \sum_{i=1}^{n} N_{ir}\bar{H}_i = -k_{\rm H}\frac{{\rm d}T}{{\rm d}r} + \sum_{i=1}^{n} N_{ir}\bar{C}_{pi}(T - T_{\rm ref}) \quad (5)$$

where we have used the reference temperature $T_{\rm ref}$ for the determination of the constituent molar enthalpies.

It is convenient to define for the three geometries, a characteristic length for transfer, $l$, taking the interface curvature into account; see Figure 1. In terms of the dimensionless distance $\eta$ (see Figure 1) we have

$$dr = (r/r_0)^\nu l \, d\eta \quad (6)$$

and it is possible to rewrite eq 5 in the convenient form

$$E_0 = -h\frac{{\rm d}T}{{\rm d}\eta} + h\phi_{\rm H} (T - T_{\rm ref}) \quad (7)$$

where we have further defined the heat transfer coefficient $h$

$$h = k_{\rm H}/l \quad (8)$$

and the dimensionless rate factor describing the influence of the interfacial molar fluxes

$$\phi_{\rm H} = \frac{\sum\limits_{i=1}^{n} N_{i0}\bar{C}_{pi}}{h} \quad (9)$$

The differential eq 7 can be solved for the boundary conditions $\eta = 0$, $T = T_0$; $\eta = 1$, $T = T_\delta$, to obtain the temperature profiles

$$\frac{T - T_0}{T_\delta - T_0} = \frac{\exp(\phi_{\rm H}\eta) - 1}{\exp(\phi_{\rm H}) - 1} \quad (10)$$

whence we obtain the conductive heat flux $q_0$

$$q_0 = -h\frac{{\rm d}T}{{\rm d}\eta}\bigg|_{\eta=0} = h \frac{\phi_{\rm H}}{\exp(\phi_{\rm H}) - 1} (T_0 - T_\delta) \quad (11)$$

Defining $h^\cdot \equiv q_0/(T_0 - T_\delta)$, the heat transfer coefficient under finite mass transfer conditions, we see that the Ackermann correction factor, $\Xi_{\rm H} \equiv h^\cdot/h$, takes the form

$$\Xi_{\rm H} = \frac{\phi_{\rm H}}{\exp(\phi_{\rm H}) - 1} \quad (12)$$

*identical* for the three geometries under consideration. The dependence of the Ackermann correction factor on the geometry, as concluded by Kalson (1983), is a direct consequence of his definition of the heat transfer coefficient using eq 2. With proper account taken for the differing curvatures and use of the generalized definition (8) we obtain the much more physically satisfying result that the Ackermann correction factor has the same form in the three geometries considered. In the limiting case that the radius $r_0$ is very much smaller than $r_\delta$, for either cylindrical or spherical geometry, it can be seen that the characteristic length $l$ reduces to $r_0$ and the Nusselt, defined as $Nu = h\cdot 2r_0/k_{\rm H}$ is equal to $2\Xi_{\rm H}$. In the further simplified situation in which the interfacial fluxes $N_i$ are vanishingly small, the classic result $Nu = 2$ is obtained.

We can generalize the result to describe the effect of the interfacial molar fluxes on the mass transfer coefficients. Let us first consider an $n$-component ideal gas mixture. The constitutive relations are most conveniently expressed in terms of the Maxwell-Stefan equations

$$\frac{{\rm d}x_i}{{\rm d}r} = \sum_{j=1}^{n} \frac{x_i N_j - x_j N_i}{c_t D_{ij}} \quad (i = 1, 2, ..., n) \quad (13)$$

Only $n - 1$ of the above equations are independent and in order to determine the $n$ interfacial fluxes we need to have an additional relationship. This additional relationship usually takes the form of a linear dependence between the fluxes

$$\sum_{i=1}^{n} \lambda_i N_i = 0 \quad (14)$$

For example for equimolar diffusion we have $\lambda_1 = \lambda_2 = ... = \lambda_n$; for diffusion of $n - 1$ species through a stagnant $n$th component, $N_n = 0$, and so $\lambda_1 = \lambda_2 = ... = \lambda_{n-1} = 0$, $\lambda_n \neq 0$. For distillation the $\lambda_i$ can be identified with the molar latent heats of vaporization of the component species.

To proceed further with the solution of the differential equations (13) as applied to planar, cylindrical, and spherical geometries, it is convenient as for the heat transfer case to define the characteristic length $l$ and the dimensionless distance $\eta$. With these definitions the set of $n - 1$ independent differential equations (13) can be cast into $n - 1$ dimensional matrix notation

$$\frac{{\rm d}(x)}{{\rm d}\eta} = [\Phi](x) + (\zeta) \quad (15)$$

where we define the matrix of dimensionless mass transfer rate fractors $[\Phi]$ by

$$\Phi_{ii} = \frac{N_{i0}}{c_t D_{in}/l} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{N_{k0}}{c_t D_{ik}/l} \quad (i = 1, 2, ..., n - 1) \quad (16)$$

$$\Phi_{ij} = -N_{i0}(l/D_{ij} - l/D_{in})/c_t$$
$$(i, j = 1, 2, ..., n - 1; i \neq j) \quad (17)$$

The matrix differential equation can be solved for the boundary condition $\eta = 0$, $(x) = (x_0)$; $\eta = 1$, $(x) = (x_\delta)$ to give the composition profile

$$(x - x_0) = [\exp[[\Phi]\eta] - [I]] [\exp[\Phi] - [I]]^{-1} (x_\delta - x_0) \quad (18)$$

which is the analogue of eq 10. The $n - 1$ independent interfacial fluxes can be conveniently represented in matrix notation as

$$(N) = c_t[\beta][B]^{-1}[\Xi] (x_0 - x_\delta) \quad (19)$$

where we have further defined two coefficient matrices $[\beta]$

and $[B]$. $[\beta]$ is the bootstrap matrix and is calculable from the $\lambda_i$'s

$$\beta_{ij} = \delta_{ij} - x_i \left( \frac{\lambda_i - \lambda_n}{\sum\limits_{l=1}^{n} x_l \lambda_l} \right) \quad (i, j = 1, 2, ..., n-1) \quad (20)$$

The matrix $[B]$ of inverted mass transfer coefficients is given by

$$B_{ii} = \frac{x_i}{D_{in}/l} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_k}{D_{ik}/l} \quad (i = 1, 2, ..., n-1) \quad (21)$$

$$B_{ij} = -x_i(l/D_{ij} - l/D_{in}), \quad (i, j = 1, 2, ..., n-1; i \neq j) \quad (22)$$

In eq 19 $[\Xi]$ represents an $n - 1$ dimensional square matrix of mass transfer correction factors

$$[\Xi] = [\Phi] [\exp[\Phi] - [I]]^{-1} \quad (23)$$

which is the analogue of eq 12. When each individual flux $N_i$ tends to vanish, $[\Xi]$ tends to the identity matrix $[I]$. Further discussion on the calculation of the fluxes $N_i$ using eq 19 can be found in Krishna and Standart (1976).

The above analysis for mass transfer in ideal gas mixtures can be extended to nonideal fluid mixtures provided the Maxwell–Stefan diffusion coefficients $D_{ij}$ can be considered to be constant over the diffusion path (this is exactly true for ideal gas mixtures for which $D_{ij}$ are composition independent). A further assumption which requires to be made is the constancy of thermodynamic correction factors $\Gamma_{ij}$, defined by

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \quad (i, j = 1, 2, ..., n-1) \quad (23)$$

which implies some averaging over the diffusion path. With these two key assumptions (constant $D_{ij}$ and $\Gamma_{ij}$), the solution for the interfacial fluxes $N_i$ can be obtained in the following convenient form

$$(N) = c_t[\beta][B]^{-1}[\Gamma][\Xi](x_0 - x_\delta) \quad (24)$$

where the Ackermann correction factor $[\Xi]$ now takes the form

$$[\Xi] = [\theta] [\exp[\theta] - [I]]^{-1} \quad (25)$$

with with $[\theta]$ defined by

$$[\theta] = [\Gamma]^{-1} [\Phi] \quad (26)$$

The application of eq 24 to the calculation of interfacial transfer fluxes in vapor–liquid and liquid–liquid systems is discussed by Krishna (1977, 1979); note that the definition of $l$ for the spherical geometry in Krishna (1977) is not as convenient as the one used in the present communication.

Finally, we would like to remark that though the derivation of the Ackermann correction factor, $\Xi_H$ or $[\Xi]$, has been on the assumption of a model assuming molecular diffusion control, formally identical expressions result even when turbulent eddy transfer phenomena are additionally taken into account; see Krishna (1982).

By proper definition of the characteristic length of the diffusion path for planar, cylindrical, and spherical geometries, we have shown that the Ackermann correction factor for heat transfer $\Xi_H$ is independent of geometry, a physically pleasing result in contrast to the findings of Kalson

(1983). The analysis can be extended to the effects of finite mass transfer rates on the mass transfer coefficients and the results presented in this paper demonstrate the generality of the original Ackermann (1937) analysis.

## Nomenclature

$[B]$ = matrix of inverted mass transfer coefficients, $m^{-1}$ s
$c_t$ = mixture molar density, kmol $m^{-3}$
$\bar{C}_{pi}$ = molar heat capacity of component $i$, J $kmol^{-1}$
$D_{ij}$ = Maxwell–Stefan diffusion coefficient for pair $i$–$j$ in a multicomponent mixture, $m^2$ $s^{-1}$
$E$ = interfacial energy flux, W $m^{-2}$
$h$ = heat transfer coefficient under conditions of vanishingly small mass transfer fluxes, W $m^{-2}$ $K^{-1}$
$\bar{H}_i$ = partial molar enthalpy of comonent $i$, J $kmol^{-1}$
$[I]$ = identity matrix
$k_H$ = thermal conductivity, W $m^{-1}$ $K^{-1}$
$l$ = characteristic diffusion path length; see Figure 1, m
$n$ = number of components in the mixture
$N_i$ = interfacial molar flux of component $i$ in a laboratory fixed coordinate reference frame, kmol $m^{-2}$ $s^{-1}$
$Nu$ = Nusselt number
$q$ = conductive heat flux, W $m^{-2}$
$r$ = coordinate direction, m
$r_0$ = inner edge of diffusion path, m
$r_\delta$ = outer edge of diffusion path, m
$x_i$ = mole fraction of component $i$
$x_{i0}$ = mole fraction of component $i$ at $r = r_0$
$x_{i\delta}$ = mole fraction of component $i$ at $r = r_\delta$

*Greek Letters*

$[\beta]$ = bootstrap matrix
$\gamma_i$ = activity coefficient of component $i$ in solution
$[\Gamma]$ = matrix of thermodynamic factors
$\delta$ = film thickness, m
$\delta_{ik}$ = Kronecker delta
$(\zeta) = \zeta_i = -N_i l/c_t D_{in}$
$\eta$ = dimensionless distance
$[\theta]$ = defined by eq 26
$\lambda_i$ = coefficients in the linear dependence relationship (14)
$\mu_i$ = molar chemical potential of species $i$, J $kmol^{-1}$
$\nu$ = parameter, = 0 for planar, = 1 for cylindrical, = 2 for spherical geometries, respectively
$[\Xi]$ = Ackermann correction factor for mass transfer coefficients
$\Xi_H$ = Ackermann correction factor for heat transfer coefficients
$\phi_H$ = dimensionless heat transfer rate factor
$[\Phi]$ = dimensionless matrix of mass transfer rate factors

*Matrix Notation*

( ) = $n - 1$ dimensional column matrix
[ ] = $n - 1 \times n - 1$ dimensional square matrix
[ ]$^{-1}$ = inverted matrix

*Superscripts*

0 = referring to position $r = r_0$
$\delta$ = referring to position $r = r_\delta$
H = parameter pertaining to heat transfer

Superscripts

· = coefficient obtained under conditions of finite mass transfer rates

## Literature Cited

Ackermann, G. *Ver. Deut. Ing. Forschungsh.* **1937**, *1*, 1.
Kalson, P. A. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 355.
Krishna, R.; Standart, G. L. *AIChE J.* **1976**, *22*, 383.
Krishna, R. *Chem. Eng. Sci.* **1977**, *32*, 659.
Krishna, R. *Chem. Eng. Commun.* **1979**, *3*, 29.
Krishna, R. *Chem. Eng. J.* **1982**, *24*, 163.

*Berliozlaan 4*                                          **Rajamani Krishna**
*2102 EE Heemstede*
*The Netherlands*