LETTERS TO THE EDITOR

TO THE EDITOR:

Recently the concept of independent reactions has been discussed in this journal by Whitwell and Dartt (1974), Björnbom (1974), and Schubert (1974). Schubert criticized Whitwell and Dartt for "unnecessary complication of a problem which was solved long ago."

I wish to point out that Schubert's history writing is misleading since the problem with the number of independent reactions was not solved long ago. It is more correct to say that confusion has existed about this problem for a long time.

It is true that Whitwell and Dartt's way of counting the number of species in systems with isomers is not the best one; instead every isomer should be taken as a separate component. However, their examples are of great interest since they show that real systems with isomers exist where the independent reactions are fewer than calculated by the rank method (regardless of the way of counting the number of species).

The first discussion of the independent reactions and the related independent components by algebraic means was made by Jouguet (1921). The formula matrix or element-by-species matrix was introduced by Brinkley (1946) who essentially derived the rank method. Prigogine and Defay (1947) criticized Brinkley's method on the grounds that all the reactions obtained in this way might not occur in reality. Jouguet's method should be used since it starts from those reactions which really occur. However, Peneloux (1947) also made an analysis and concluded that there is no essential difference between those two methods. They give always the same number of independent reactions if inert components are not considered in the element-by-species matrix.

This discussion in the literature seems to have influenced later workers concerned with independent reactions in calculation of complex chemical equilibria. Hence Zeleznik and Gordon (1968) indicate that Brinkley's method can be used without discussing the possibility that not all the reactions obtained might occur. This is in contrast to Aris and Mah (1963) who maintain that the number of independent reactions actually taking place should be determined empirically and that the rank method gives only an upper limit.

Probably two difficulties in stoichiometric theory have contributed to these contradictions. One is connected with the expression "the reactions which really occur." However, in stoichiometry we are concerned with reactions which describe the composition changes in the system, but these reactions do not necessarily occur as elementary steps.

For example, in the propane oxidation example (Björnbom, 1974), none of the six reactions which describe the system occurs as an elementary step. Moreover, it is not possible to find any set of reactions between the components in this system which represent the real elementary steps. The latter steps include species such as free radicals which we do not consider in connection with the stoichiometric behavior of the system.

Hence, it is often meaningless to discuss "the reactions which really occur in the system," but in stoichiometry the problem is to find one of infinite many equivalent sets of independent reactions which describe the stoichiometric behavior.

The second difficulty is that the number of independent reactions need not be unique. If this number is not unique, the sets of independent reactions obtained by the rank method will describe the stoichiometric behavior as well as some sets with fewer independent reactions. However, the sets obtained from the rank method do not give a correct account of the degrees of freedom in the system and cannot be used for complex equilibrium calculations. A detailed analysis is given elsewhere (Björnbom, 1975).

With this background, examples such as those of Whitwell and Dartt and Björnbom (1974) are of great interest since they show that real cases can occur when the independent reactions sufficient to describe the stoichiometric behavior are fewer than indicated by the rank method.

Moreover, these examples prove that the analysis by Peneloux is not correct. In general, it is not correct to find the independent reactions for equilibrium calculations from the rank method without inert components.

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TO THE EDITOR:

We have found several errors in the paper by Chandrasekhar and Hoelscher (1975). The first, and most fundamental, is their neglect of the distribution coefficient in their model for diffusion of a solute between phases. Their first boundary condition (unnumbered) for $0 < t < \infty$, $x = 0$, should read

$$D_1 \frac{\partial C_1}{\partial x} - h(C_1 - C_2/m) = 0 \quad (1)$$

where m is the distribution coefficient, C_2/C_1, at equilibrium.

For infinite-length two-phase systems this leads to the concentration gradient at the interface:

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = \frac{C_0}{\left[1 + m\left(\frac{D_2}{D_1}\right)^{1/2}\right]} \left\{ m\left(\frac{D_2}{D_1}\right)^{1/2} (\pi D_1 t)^{-1/2} \right\} \quad (2)$$

for the case of negligible interfacial resistance, and m independent of C. The distribution coefficient for the system water-acetic acid-toluene ranges from about 0.025 to 0.04 (Lewis, 1954) in the concentration range investigated. Our Equation (2) will show a linear response of $(\partial C_1/\partial x)_{x=0}$ to $t^{-1/2}$ as does Equation (3) of C-H, only if m is assumed constant.

For the case of significant interfacial resistance we obtain

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = \frac{C_0 h_1}{\left[\left(\frac{D_2}{D_1}\right)^{1/2} + \frac{1}{m}\right]} (D_2/D_1)^{1/2} \{1 - 2h_1(D_1 t/\pi)^{1/2} + \ldots\} \exp(D_1 t h_1^2) \quad (3)$$

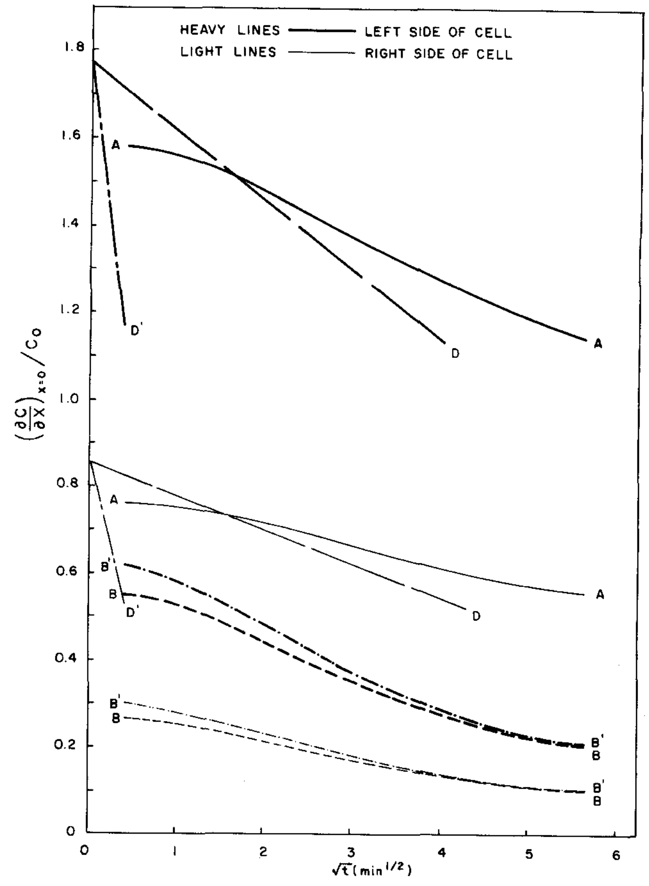
$$\left(\frac{\partial C_2}{\partial x}\right)_{x=0} = \frac{C_0 h_2}{\left[\left(\frac{D_2}{D_1}\right)^{1/2} + \frac{1}{m}\right]} \{1 - 2h_2(D_2 t/\pi)^{1/2} + \ldots\} \exp(D_2 t h_2^2) \quad (4)$$

where h_1 and h_2 are defined analogous o those of C-H:

$$h_1 = \frac{h}{D_1}[(D_1/D_2)^{1/2}/m + 1]$$

$$h_2 = \frac{h}{D_2}\left[(D_2/D_1)^{1/2} + \frac{1}{m}\right]$$

f the value of h reported by C-H is used, the exponential term is non-egligible, giving rise to curves instead f the straight line shown in their Figre 6. Equations (3) and (4) above will yield a value for h about twenty-ve percent smaller in the water-acetic acid-toluene system than that reported by C-H. The fit, because of the reasons just described, is not good.



Legend

Curve	a, cm	m	h⁺, cm/sec	model
A	1.0	1.0	2.0×10^{-5}	finite-length
B	1.0 1.5	0.04	2.0×10^{-5}	finite-length
B′	1.0 1.5	0.04	2.0×10^{-2}	finite-length
D	∞	1.0	2.0×10^{-5}	infinite-length
D′	∞	0.04	2.0×10^{-5}	infinite-length

⁺ *h* of 2.0×10^{-5} cm/sec corresponds approximately with the value reported by C-H for water-acetic acid-toluene.
h of 2.0×10^{-2} cm/sec (or larger) corresponds to insignificant interfacial resistance.

Secondly, however, the use of the infinite-length assumption is apparently not justified here. The complete analysis of a finite-length two-phase system is available (Scott, et.al., 1951). The concentration gradients at $x = 0$ are found from series solutions involving C_0, D_1, D_2, h, m, t, and a, the half-length of the diffusion cell. We do not present them here due to their length. We have made calculations using the first ten terms of the series and present them in Figure 1 along with those from Equations (3) and (4). The ordinate, $(\partial C/\partial x)_{x=0}/C_0$, is proportional to Y' of C-H. We cannot make an exact comparison without more complete information. Some conclusions that can be drawn from the results are

1) Although we do not know the exact length of the diffusion cell, calculations with 1.0 and 1.5 cm. gave essentially identical curves.

2) Comparing D and D', we see that, even within the infinite-length model, the slope is greatly affected by the value of m used. For the water-acetic acid-toluene system, m is quite variable, as we have noted.

3) All finite-length-model results are curved.

4) When an approximately correct value of m is used in the correct, finite-length model, curves B and B' (significant and insignificant interfacial resistance) approach each other. This would make it difficult to ascertain the value of h_1 even if m were constant. Thus the conclusion of C-H that there was a significant interfacial resistance in one of their systems, in variance with the results of Ward and Quinn (1965), is illusory.

5) The results for the finite-length model depart drastically from those of

the infinite-length model.

We have not examined the other immiscible systems tested by C-H, but we suggest these results may also be in error.

Recent measurements by Harada (1975) on mass transfer of carboxylic acids across the water-benzene interface indicate that the interfacial resistance increases markedly with the number of CH_2 groups. For acetic acid as a solute, however, no detectable resistance was observed. For propionic acid, the resistance is on the order of 10^2 sec/cm which is about two orders of magnitude smaller than the value reported by C-H for water-toluene. It is highly unlikely that the benzene-water and toluene-water interfaces would behave much differently toward the transfer of a third component.

Our third comment regards the effect of the sedimentation force. For the right side of the diffusion cell (Cullinan and Lenczyk, 1969),

$$\partial C_1/\partial t = D_1 \left[\frac{\partial^2 C_1}{\partial x^2} - \frac{(M_1 - \rho V_1)\omega^2}{\partial \mu_1/\partial C_1} \right] \quad (5)$$

A similar expression is obtained for the left side. If we make the assumption, for a first-order calculation, that acetic acid-water can be described as an ideal mixture,

$$\frac{\partial \mu_1}{\partial C_1} = RT/C_1$$

and, using the appropriate values for M_1, ρ, V_1, and ω, the second term on the RHS is about $-0.066\ C_1$ g-moles/(c.c.)(cm^2). The first term on the RHS can be determined from the solution shown by Crank, p. 38, (1956). We use here $x = 0.5$ cm, $t = 360$ sec., and $h = 2 \times 10^{-5}$ cm/sec. We find $\partial^2 C_1/\partial x^2 \cong 2 \times 10^{-5}\ C_0$ g-moles/(c.c.)(cm^2).

Thus, for $C_1 \cong 0.5\ C_0$, the sedimentation effect is comparable to that of diffusion. Accurate assessment would be difficult.

Fourth, the consistency of the data on miscible systems is somewhat questionable. For glycol-water at 25°C, at $\theta = 80°$ and 70° respectively, $D_1 = 1.55 \times 10^{-5}$ cm^2/sec and 1.53×10^{-5} cm^2/sec. While these results are self-consistent, they deviate about 30% from the accepted value of 1.15×10^{-5}. At 15°C, however, the values of D_1 at the two schlieren angles are 1.36×10^{-5} (83°) and 0.96×10^{-5} (75°), only roughly averaging to the value shown in Table 1 of C-H (1.26×10^{-5}).

Finally, the procedure used to calculate (dn/dc) may be in serious error. In the sample calculation shown, (C-H, p. 108) the (dn/dc) for propionic acid in toluene is assumed to be:

$$\frac{dn}{dc} = (n_{\text{toluene}} - n_{\text{propionic acid}})/100 = \frac{(1.4961 - 1.3868)}{100} = 1.1 \times 10^{-3}/\text{wt.}\%$$

We were not able to find data on this mixture, but for water-acetic acid, (Timmermans, 1960) over the range, 0-10 wt% acetic acid, $(\Delta n/\Delta c) \cong 7.19 \times 10^{-4}$/wt.%. However, when the slope is calculated from the indices of the pure components, as C-H apparently have done, $(\Delta n/\Delta c) = 3.95 \times 10^{-4}$/wt.%. Even if the more reasonable mole percent instead of weight percent had been used, the non-ideality of these systems precludes assumption of linearity over the entire concentration range.

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TO THE EDITOR:

This is in reply to the letter from Huang and Winnick re our paper entitled "Mass Transfer Studies Across Liquid/Liquid Interfaces," *AIChE J.*, 21, 103 (1975).

(1) All data providing the basis for this study were obtained within 1 mm of the interface. The photographic evidence obtained indicates clearly and unequivocally that the concentration was not constant on either side of the interface but, rather, approached the equilibrium value of 1/2 C_0 relatively slowly. Reference should be made to Crank (1956), equation (3.48), not to equation (3.41).

$$\text{at} \quad x = 0, \quad C_2/C_1 = k \qquad (3.41)$$

$$\text{at} \quad x = 0, \quad D\frac{\partial C_1}{\partial x} + h(C_2 - C_1) = 0 \qquad (3.48)$$

The former is for those cases having no contact resistance at $x = 0$. The latter is for those cases having a non-zero contact resistance at $x = 0$.

Having succeeded in obtaining Schlieren data in the immediate vicinity of the interface, we suggest that it is proper to dispense with the notion of a distribution coefficient. If we had not succeeded in working within 1 mm of the interface, then we would have been tempted to use the notion of a distribution coefficient in our analysis. An examination of Figure 5a and 5b in our paper will make this point clear.

(2) It is true that the results of our indicating an interfacial region thickness of the order of 0.1 mm . . . . perhaps, better, the region of an interphase . . . . are at variance with conventional thinking indicating that the interface is of the order of 10 Å thickness. However, our results derive from photographic data which are difficult to explain in any other way. The nature of the experiments performed was such that any intruding factors (temperature inequalities, temperature transients, etc.) made it impossible to obtain any results. To question the visual results obtained to date during the study, one must be prepared to offer an alternate explanation for the photographic evidence. However, we suggest that an even more important result is to call attention to the fact that one *can* obtain precise interfacial concentration data at distances within 1 mm of the interface using commercially available instrumentation.

(3) There is a printing error in our paper. Equation (5) should read:

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = \frac{(D_2/D_1)^{1/2}}{1 + (D_2/D_1)^{1/2}} C_0 h_1 \left[1 - \frac{2h_1}{\sqrt{\pi}} \sqrt{D_1 t} \right]$$

We are grateful to Drs. Huang and Winnick for calling this to our attention.

(4) The maximum mass flux seems clearly to occur at the point where the concentration gradient is maximum as evident from the photographs. The fact that this occurs at some distance from the "interface" is indeed curious and is unexplained but does seem clearly indicated by the data obtained.

(5) We suggest that there is no serious error in the calculation procedure for estimating *dn/dc*. The only assumption made which is of fundamental relevance to the published results is the existence of a linear relationship between *n* and *c*. This seems totally reasonable at the concentration levels used in the study. The assumption of "infinite length" is made reasonable by the observation that the solute has not reached the outer boundary of either phase during the period of the experiments. See, particularly, Figure 7. Finally, the fact that experimental values for the diffusion coefficient obtained using the centrifuge check reasonably well with those reported in the literature from other more classical studies seems clearly to indicate the absence of a "sedimentation effect" . . . . at least within the limits of these results. "Sedimentation" must thus be considered negligible by comparison with diffusion.

It seems worth repeating that the credibility of our results rests on the photographic evidence which provide the basis for the observations made. We acknowledge that some results seem at variance with ideas commonly accepted in the literature of interfacial mass transfer. We would be pleased to see our work repeated and comparisons made.

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Reply submitted by H. E. Hoelscher for both authors.

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Chandrasekhar, S. and H. E. Hoelscher, "Mass Transfer Studies Across Liquid/Liquid Interfaces", *A.I.Ch.E. J.*, **21**, 103 (1975).

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TO THE EDITOR:

In a recent R. & D. Note, "The Functionally Near-Equivalency of Reynolds and Grashof Numbers, *AIChE Journal*, **21** (3), 609-610 (1975) Niels Madsen suggests that the Reynolds number and the square root of the Grashof number are nearly functionally equivalent. He further suggests that vectorial addition of *Re* and *Gr′* may provide a way of predicting mixed free and forced convection. This near-equivalence was first suggested by Krischer and Loos (1958) and later by Tsubouchi and Sato (1960). The latter authors and Börner (1965) tried to use vectorial addition in correlating their mixed convection data with poor results in opposing flow. Much evidence is now available from which it can be concluded that vectorial addition is unsatisfactory, e.g. the theoretical studies of Sparrow *et al.* (1959) and Merkin (1969) and the experimental work of Garner and Hoffmann (1961), Pei (1965), Narasimhan and Gauvin (1967) and Wilhelm (1971). It is also clear from flow visualization studies (Börner, 1965; Wilhelm, 1969) that the postulate of vectorial addition gives no insight into the complex flow patterns in mixed convection. Additional effort should be directed to furthering our basic understanding of mixed flows rather than along the lines suggested in Madsen's note.

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TO THE EDITOR:

The remarks above concerning my *R&D Note* focuses attention on the past effort that has been expended by many investigators on the problem of mixed convection, either theoretical (boundary-layer analysis) or empirical (data correlation). My approach was limited to dimensional analysis supported by experimental data from the literature. In an earlier paper Lemlich and Hoke treated the same problem with a somewhat similar result and introduced the concept of an "equivalent velocity" for natural convection heat transfer. To summarize: (1) In my note the "equivalent velocity" is equal to $(\Delta t \beta g L)^{1/2}$ and it is shown on Fig. 1 that using this velocity, in the usual expressions for the heat-transfer coefficient for air in cross flow over a horizontal cylinder, yields nearly the same results for both natural and forced convection. In this connection, the figure, Fig. 1, should have been labeled $\log_{10} \overline{\mathrm{Nu}}$ vs $\log_{10} (Re \cdot Pr^{1/2})$. 2) The dimensionless ratio Gr/Re^2 used by Tanaev (1956), Acrivos (1958) and Sparrow *et al.* (1959) is basically the square of the dimensionless ratio "effective velocity" over the forced velocity.

In conclusion, the "effective velocity" is a useful parameter in the theoretical analysis of natural and mixed natural and forced convection, but the literature cited by Weber indicates that simple vector addition appear not generally to be an adequate treatment of the mixed heat transfer problem.

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ERRATA

(Continued from page 203)

In the paper "Extensional Viscosity and Recoil in Highly Dilute Polymer Solutions" by Chander Balakrishnan and R. J. Gordon, 21, 1225 (1975), the word "left" in the caption to Fig. 1 should be changed to "right."